FAST-ACTING FORMULATION COMPONENTS, COMPOSITIONS AND LAUNDRY METHODS EMPLOYING SAME

Field of the Invention

The present invention relates to formulation components, such as organic catalyst compounds designed with time-controlled bleaching to increase color safety, compositions and laundry methods employing such organic catalyst compounds. More particularly, this invention relates to organic catalysts compounds such as quaternary imine bleach boosting compounds, quaternary oxaziridinium bleaching species, modified amines and amine oxides, imines, and/or oxaziridines, compositions and laundry methods employing such organic catalyst compounds.

Background of the Invention

Oxygen bleaching agents have become increasingly popular in recent years in household and personal care products to facilitate stain and soil removal. Bleaches are particularly desirable for their stain-removing, dingy fabric cleanup, whitening and sanitization properties. Oxygen bleaching agents have found particular acceptance in laundry products such as detergents, in automatic dishwashing products and in hard surface cleansers. Oxygen bleaching agents, however, are somewhat limited in their effectiveness. Some frequently encountered disadvantages include their lack of fabric color safety and their tendency to be extremely temperature rate dependent. Thus, the colder the solution in which they are employed, the less effective the bleaching action. Temperatures in excess of 60 °C are typically required for effectiveness of an oxygen bleaching agent in solution.

To solve the aforementioned temperature rate dependency, a class of compounds known as "bleach activators" has been developed. Bleach activators, typically perhydrolyzable acyl compounds having a leaving group such as oxybenzenesulfonate, react with the active oxygen group, typically hydrogen peroxide or its anion, to form a more effective peroxyacid oxidant. It is the peroxyacid compound which then oxidizes the stained or soiled substrate material. However, bleach activators are also somewhat temperature dependent. Bleach activators are more effective at warm water temperatures of from about 40 °C to about 60 °C. In water temperatures of less than about 40 °C, the peroxyacid compound loses some of its bleaching effectiveness.

Unsuccessful attempts have been made, as disclosed in U.S. Patent Nos. 5,360,568, 5,360,569 and 5,370,826 all to Madison et al., to develop a bleach system comprising organic catalysts, more specifically, iminium-based organic catalysts, which is effective in lower

temperature water conditions and is safe on colors. However, cationic, quaternary imine salts, one of the types of organic catalysts disclosed in these applications, are not completely satisfactory in laundry bleaching applications. In particular, the quaternary imine salts, when combined with peroxygen compounds, cause an unacceptable level of color damage on fabrics.

U.S. Patent Nos. 5,576,282 and 5,817,614 both to Miracle et al. disclose another attempt at developing a bleach system comprising organic catalysts which is effective in lower temperature water conditions and is relatively safe on colors. Although the bleach system disclosed in this patent provides enhanced color-safety over the traditional organic catalyst bleach systems, consumers desire more color-safe bleach products.

Additional disadvantages associated with the conventional organic catalysts, examples of which are described in U.S. Patent Nos. 5,360,568, 5,360,569 and 5,370,826 all to Madison et al., and U.S. Patent Nos. 5,576,282 and 5,817,614, both to Miracle et al., include the organic catalysts having prolonged activity. Iminiums and dihydroisoquinoliniums, and the quaternary oxaziridinium bleaching species formed from them, exemplified in the art have organic catalyst lifetimes about greater than 15 min at 20 °C, as determined according to the Test Protocol, disclosed hereinafter. Such stability can result in too much available oxygen ("AvO") consumption, leading to an altered performance profile (i.e., changing the balance between peracid bleaching and organic catalyst bleaching).

In light of the foregoing, it is evident that there still exists a need for an organic catalyst bleach system that provides effective bleaching in lower temperature water conditions and provides time-controlled bleaching and superior color-safety properties compared to the bleach systems disclosed in the prior art.

Summary of the Invention

The present invention fulfills the need discussed above. The present invention provides formulation components, such as organic catalyst compounds having an effective lifetime of less than 20 minutes and greater than 15 seconds at 20 °C under the conditions outlined in Test Protocol I described hereinafter. Such organic catalyst compounds work best in lower wash temperatures less than 80 °C.

In addition to the organic catalyst compounds, compositions and laundry methods employing such organic catalyst compounds are also disclosed herein. More particularly, organic catalysts compounds such as quaternary imine bleach boosting compounds, quaternary oxaziridinium bleaching species, modified amines and amine oxides, imines and oxaziridines, compositions and laundry methods employing such organic catalyst compounds are provided by the present invention.

Nonlimiting examples of the benefits provided by the formulation components, specifically the organic catalyst compounds, include superior bleaching effectiveness even in lower temperature water, and improved color safety.

In one aspect of the present invention, a formulation component, preferably an organic catalyst compound which demonstrates effective bleaching in lower water temperature and provides a superior color-safety profile compared to the conventional organic catalyst is provided.

In accordance with another aspect of the present invention, a bleaching composition comprising one or more of the formulation components described above in conjunction with or without a peroxygen source is provided.

In accordance with yet another aspect of the present invention, a method for laundering a fabric in need of laundering comprising contacting the fabric with a laundry solution having one or more of the bleaching compositions described herein is provided.

In accordance with still yet another aspect of the present invention, a laundry additive product comprising one or more of the formulation components described herein is provided.

Accordingly, it is an object of the present invention to provide: a formulation component, preferably an organic catalyst compound, which demonstrates improved performance even in lower temperature water solutions and improved color safety; a bleaching composition comprising one or more of the formulation components described herein; a method for laundering a fabric using one or more of the bleaching compositions described herein; and a laundry additive product comprising one or more of the formulation components described herein.

These and other objects, features and advantages of the present invention will be recognized by one of ordinary skill in the art from the following description and the appended claims.

All percentages, ratios and proportions herein are on a weight basis unless otherwise indicated. All documents cited herein are hereby incorporated by reference.

Detailed Description of the Invention

The present invention discloses highly useful formulation components, such as organic catalyst compounds ("bleach boosting compounds", "bleaching species", "modified amines", "modified amine oxides", "imines", "oxaziridine imines"and mixtures thereof), compositions, and methods employing the formulation components.

The formulation components, particularly the organic catalyst compounds of the present invention provide increased bleaching effectiveness in lower temperature wash applications while providing improved color safety, resulting in increased bleaching effectiveness and color safety. The formulation components of the present invention act in conjunction with or without,

preferably with conventional peroxygen bleaching sources to provide the above-mentioned increased bleaching effectiveness and superior fabric color safety.

ORGANIC CATALYST COMPOUNDS

Nonlimiting examples of organic catalyst compounds, such as bleach boosting and bleaching species compounds are described in U.S. Patent Nos. 5,041,232, 5,045,223, 5,047,163, 5,310,925, 5,413,733, 5,360,568, 5,482,515, 5,550,256, 5,360,569, 5,478,357, 5,370,826, 5,442,066, 5,576,282, 5,760,222, 5,753,599, 5,652,207 and 5,817,614, PCT Published Applications WO 98/23602, WO 95/13352, WO 95/13353, WO 95/13351, WO 97/06147 and WO 98/23717, and EP 728 182.

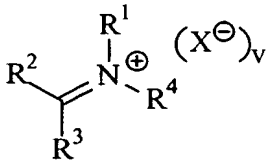
The organic catalyst compounds of the present invention and bleaching compositions (products) containing such organic catalyst compounds that are particularly useful in the methods of the present invention are the organic catalyst compounds and compositions containing same that satisfy the conditions outlined in Test Protocols I, II and/or III, disclosed hereinafter.

Preferably, the organic catalyst compounds of the present invention, more preferably the iminium-based organic catalyst compounds of the present invention, include, but are not limited to, bleach boosting compounds, modified amines, modified amine oxides, sulfonimines, phosphinimes, thiodiazole dioxides and mixtures thereof.

I. Bleach Boosting Compounds - The bleach boosting compounds, preferably iminium-based bleach boosting compounds, of the present invention include, but are not limited to, aryliminium cations, aryliminium polyions, which have a net charge of from about +3 to about -3, and aryliminium zwitterions, which have a net charge of from about +3 to about -3.

A preferred organic catalyst in accordance with the present invention and for use in the bleaching compositions of the present invention is a bleach boosting compound selected from aryliminium zwitterions or its oxaziridinium bleaching species because unlike aryliminium cations and/or oxaziridinium cations, the zwitterions provide effective bleaching without resulting in unacceptable level of color damage on fabrics.

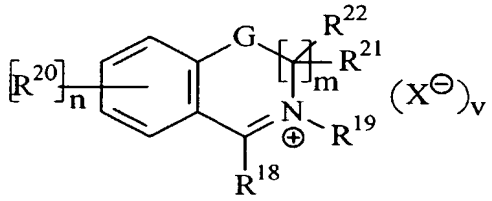
a. Aryliminium Cations and Polyions - The aryliminium cations and aryliminium polyions, which have a net charge of from about +3 to about -3, are represented by the formula [I]:



[I]

where R^2-R^3 are independently selected from substituted or unsubstituted, saturated or unsaturated radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; R^1 and R^4 are radicals selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals, provided that when R^1 or R^4 is isopropyl, R^2 or R^3 is not $ArCOCH_3$; X^{-} is a suitable charge-balancing counterion, preferably a bleach-compatible counterion; and v is an integer from 1 to 3.

Preferably, the aryliminium cations and aryliminium polyions, which have a net charge of from about +3 to about -3, are represented by the formula [XI]:



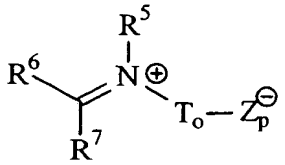
[XI]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; and n is an integer from 0 to 4; each R^{20} is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R^{20} substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring, provided that R^{20} is not phenyl; and provided that when R^{19} is isopropyl, R^{20} is not $COCH_3$; R^{18} may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; R^{19} is a radical selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl and heterocyclic ring; G is selected from the group consisting of: (1) -O- ; (2) -N(R^{23})-; and (3) -N($R^{23}R^{24}$)-; R^{21}-R^{24} are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched C_1-C_{12} alkyls, alkylenes, alkoxys, aryls, alkaryls, aralkyls, cycloalkyls, and heterocyclic rings; provided that any of R^{18}, R^{19}, R^{20}, R^{21}-R^{24} may be joined together with any other of R^{18}, R^{19}, R^{20}, R^{21}-R^{24} to form part of a common ring; any geminal R^{21}-R^{22} may combine to form a carbonyl; any vicinal R^{21}-R^{24} may join to form unsaturation; and wherein any

one group of substituents R^{21}-R^{24} may combine to form a substituted or unsubstituted fused unsaturated moiety; X^- is a suitable charge-balancing counterion, preferably a bleach-compatible counterion; v is an integer from 1 to 3.

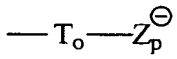
More preferred, aryliminium cations and aryliminium polyions, which have a net charge of from about +3 to about -3, as represented by the formula [XI], include those of formula [XI] where R^{18} is H or methyl and R^{19} is H or substituted or unsubstituted, saturated or unsaturated C_1 - C_{14} alkyl or cycloalkyl.

b. Aryliminium Zwitterions - The aryliminium zwitterions, which have a net charge of from about +3 to about -3, are represented by the formula [II]:



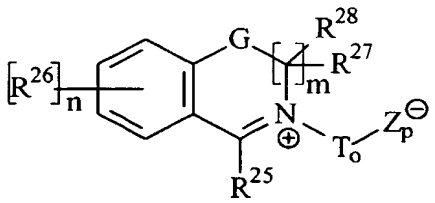
[II]

where R^5-R^7 are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; also present in this formula is the radical represented by the formula:



where Z_p^- is covalently bonded to T_o, and Z_p^- is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$ and p is either 1, 2 or 3; T_o is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl, and heterocyclic ring.

Preferably, the aryliminium zwitterions, which have a net charge of from about +3 to about -3, are represented by the formula [XII]:



[XII]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; and n is an integer from 0 to 4; each R^{26} is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R^{26} substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R^{25} may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; also present in this formula is the radical represented by the formula:

$$—T_o—Z_p^{\ominus}$$

where Z_p^- is covalently bonded to T_o, and Z_p^- is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$ and p is either 1, 2 or 3; T_o is selected from the group consisting of:

$$—(C)q—$$
(with R^{29} above and below the C)

wherein q is an integer from 1 to 8; R^{29} is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups; G is selected from the group consisting of: (1) -O- ; (2) $-N(R^{30})-$; and (3) $-N(R^{30}R^{31})-$; R^{27}, R^{28}, R^{30} and R^{31} are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of R^{25}, R^{26}, R^{27}, R^{28}, R^{30} and R^{31} may be joined together with any other of R^{25}, R^{26}, R^{27}, R^{28}, R^{30} and R^{31} to form part of a common ring; any geminal R^{27} - R^{28} may combine to form a carbonyl; any vicinal R^{27} - R^{31} may join to form unsaturation; and wherein any one group of substituents R^{27} - R^{31} may combine to form a substituted or unsubstituted fused unsaturated moiety; and provided that the radical represented by the formula:

$$—T_o—Z_p^{\ominus}$$

is not $CH_2CH(OSO_3^-)R^{41}$ wherein R^{41} is selected from the group consisting of geminal dimethyl substituted alkyl, unsubstituted alkyl and phenyl.

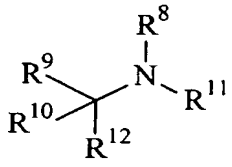
More preferred aryliminium zwitterions, which have a net charge of from about +3 to about -3, as represented by the formula [XII], include those of formula [XII] where R^{25} is H or methyl, and for the radical represented by the formula:

$$—T_o—Z_p^{\ominus}$$

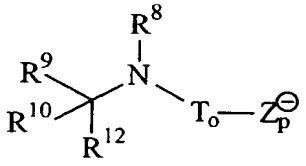
Z_p^- is $-CO_2^-$, $-SO_3^-$ or $-OSO_3^-$, and p is 1 or 2; even more preferably Z_p^- is $-SO_3^-$ or $-OSO_3^-$, and p is 1.

II. Modified Amine/Amine Oxide Compounds - The modified amine and/or amine oxide compounds of the present invention include, but are not limited to, modified amines and modified amine oxides having a net charge of from about +3 to about -3.

a. Modified Amines - The modified amines are represented by formulas [V] and [VI]:



[V]



[VI]

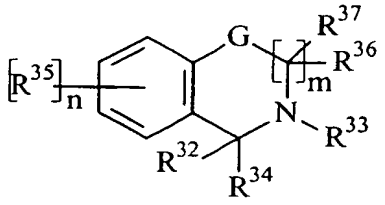
where R^9-R^{10} are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals and anionic and/or cationic charge carrying radicals; R^8 and R^{11} are radicals selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals and anionic and/or cationic charge carrying radicals; R^{12} is a leaving group, the protonated form of which has a pK_a value (H_2O reference) that falls within the following range: $37 > pK_a > -2$; with the proviso that any R^8-R^{12}, when present, may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; and the radical represented by the formula:

$$—T_o—Z_p^{\ominus}$$

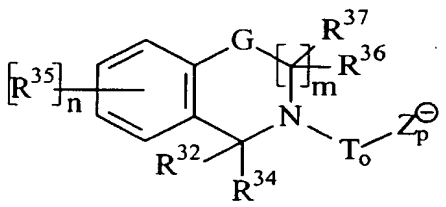
where Z_p^- is covalently bonded to T_o, and Z_p^- is selected from the group consisting of

$-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$ and p is either 1, 2 or 3; T_o is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl, and heterocyclic ring.

Preferably, the modified amines are represented by the formulas [XV] and [XVI]:

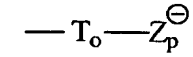


[XV]

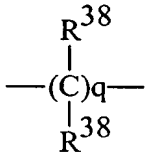


[XVI]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; and n is an integer from 0 to 4; each R^{35} is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R^{35} substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R^{32} may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; R^{33} may be a substituted or unsubstituted, saturated or unsaturated, radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, and also present in this formula is the radical represented by the formula:



where Z_p^- is covalently bonded to T_o, and Z_p^- is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$, and p is either 1, 2 or 3; T_o is selected from the group consisting of:

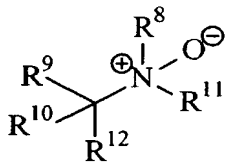


wherein q is an integer from 1 to 8; R^{38} is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups, provided that all R^{38} groups are not independently selected to be H; G is

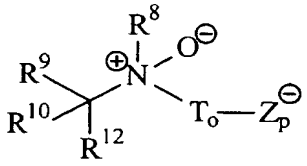
selected from the group consisting of: (1) -O- ; (2) -N(R^{39})-; and (3) -N($R^{39}R^{40}$)-; R^{36}, R^{37}, R^{39} and R^{40} are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of R^{32}, R^{33}, R^{34}, R^{35}, R^{36}, R^{37}, R^{39} and R^{40} may be joined together with any other of R^{32}, R^{33}, R^{34}, R^{35}, R^{36}, R^{37}, R^{39} and R^{40} to form part of a common ring; any geminal R^{36}- R^{37} may combine to form a carbonyl; any vicinal R^{36}, R^{37}, R^{39} and R^{40} may join to form unsaturation; and wherein any one group of substituents R^{36}, R^{37}, R^{39} and R^{40} may combine to form a substituted or unsubstituted fused unsaturated moiety.

More preferred modified amines, as represented by the formulas [XV] and [XVI], include those modified amines having a net charge of about +1 to about -1 where R^{32} is H and/or Z_p^- is -CO_2^-, -SO_3^-, or -OSO_3^-.

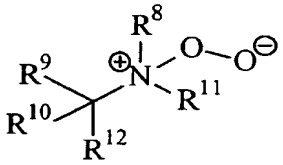
The modified amine oxides of the present invention are represented by formulas [VII]-[X]:



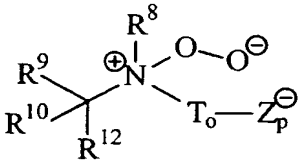
[VII]



[VIII]



[IX]



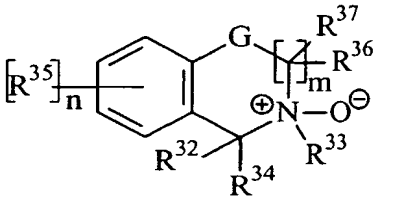
[X]

where R^8-R^{10} are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals and anionic and/or cationic charge carrying radicals; R^{11} is a radical selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals and anionic and/or cationic charge carrying radicals; R^{12} is a leaving group, the protonated form of which has a pK_a value (H_2O reference) that falls within the following range:

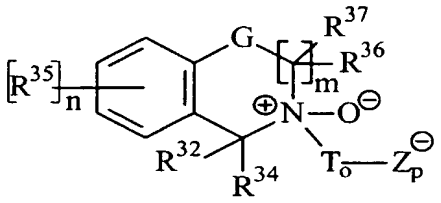
$37 > pK_a > -2$; with the proviso that any R^8-R^{12}, when present, may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; and also present in this formula is the radical represented by the formula:

where Z_p^- is covalently bonded to T_o, and Z_p^- is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$ and p is either 1, 2 or 3; T_o is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl, and heterocyclic ring.

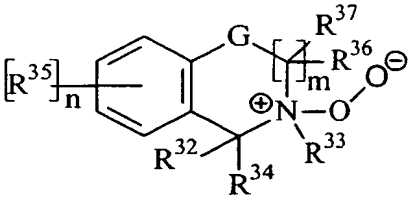
Preferably, the modified amine oxides are represented by formulas [XVII]-[XX]:



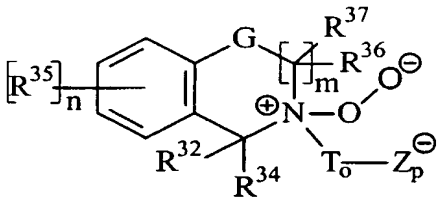
[XVII]



[XVIII]



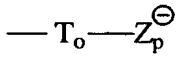
[XIX]



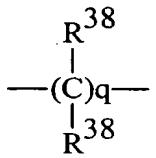
[XX]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; and n is an integer from 0 to 4; each R^{35} is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R^{35} substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R^{32} may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; R^{33} may be a substituted or unsubstituted, saturated or unsaturated, radical selected from the group consisting of

H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, and also present in this formula is the radical represented by the formula:



where Z_p^- is covalently bonded to T_o, and Z_p^- is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$, and p is either 1, 2 or 3; T_o is selected from the group consisting of:



wherein q is an integer from 1 to 8; R^{38} is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups, provided that all R^{38} groups are not independently selected to be H; G is selected from the group consisting of: (1) -O- ; (2) $-N(R^{39})-$; and (3) $-N(R^{39}R^{40})-$; R^{36}, R^{37}, R^{39} and R^{40} are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of R^{32}, R^{33}, R^{34}, R^{35}, R^{36}, R^{37}, R^{39} and R^{40} may be joined together with any other of R^{32}, R^{33}, R^{34}, R^{35}, R^{36}, R^{37}, R^{39} and R^{40} to form part of a common ring; any geminal R^{36}- R^{37} may combine to form a carbonyl; any vicinal R^{36}, R^{37}, R^{39} and R^{40} may join to form unsaturation; and wherein any one group of substituents R^{36}, R^{37}, R^{39} and R^{40} may combine to form a substituted or unsubstituted fused unsaturated moiety;

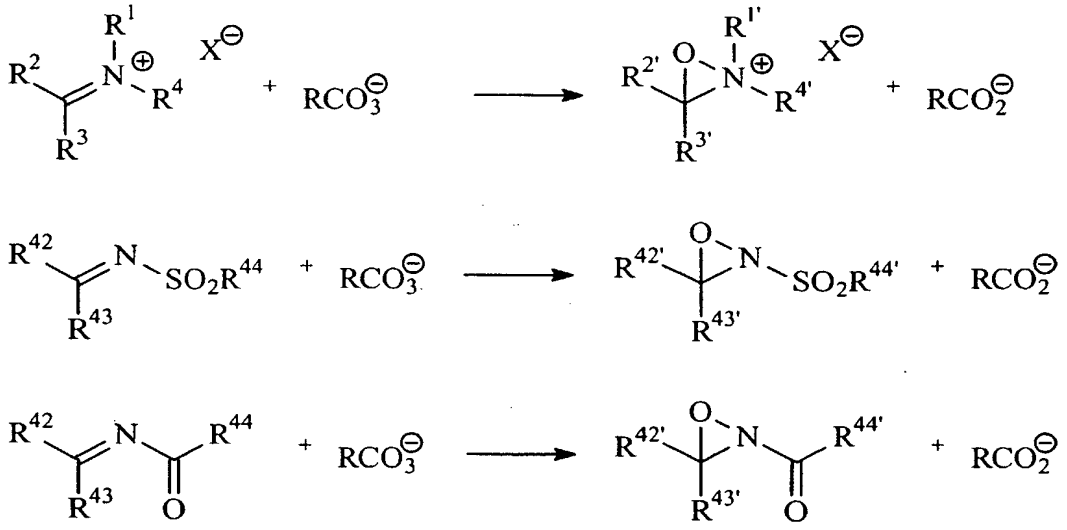
Preferred modified amines, as represented by the formulas [XVII]-[XX], include those modified amines having a net charge of about +1 to about -1 where R^{32} is H or methyl and/or Z_p^- is $-CO_2^-$, $-SO_3^-$, or $-OSO_3^-$.

For the modified amine compounds, R^{12} is a leaving group (LG), the protonated form of which has a pK_a value (H_2O reference) that fall within the following range: $37 > pK_a > -2$; preferably $30 > pK_a > 0$; more preferably $23 > pK_a > 3$; even more preferably $17 > pK_a > 11$; most preferably R^{12} is a leaving group consisting of substituted or unsubstituted, saturated or unsaturated hydroxy, perhydroxy, alkoxy and peralkoxy radicals, and any R^8-R^{12} may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring.

III. Bleaching Species - The bleaching species (oxaziridiniums, oxaziridines) may also be used directly in accordance with the present invention. The bleaching species of the present

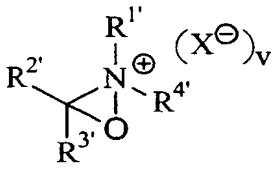
invention include, but are not limited to, oxaziridinium cations, oxaziridinium polyions, which have a net charge of from about +3 to about -3, oxaziridinium zwitterions, which have a net charge of from about +3 to about -3, oxaziridine sulfonimines, oxaziridine phosphonimines, oxaziridine thiodiazole dioxides, and mixtures thereof.

The organic catalysts, especially the aryliminium cations, aryliminium polyions, aryliminium zwitterions, sulfonimines, phosphonimines, thiodiazole dioxides of the present invention act in conjunction with a peroxygen source, when present to increase bleaching effectiveness. Without being bound by theory, it is believed that the organic catalysts react with the peroxygen source to form a more active bleaching species, a quaternary oxaziridinium and/or oxaziridine compounds, as represented by the following reaction by way of example:



The oxaziridinium and/or oxaziridine compounds can have an increased or preferred activity at lower temperatures relative to the peroxygen compound.

a. Oxaziridinium Cations and Polyions - The oxaziridinium cations and polyions, which have a net charge of from about +3 to about -3, are represented by the formula [III]:

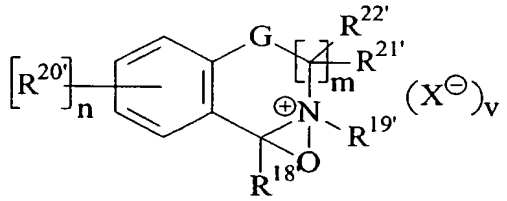


[III]

where $R^{2'}$-$R^{3'}$ are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro,

halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; $R^{1'}$ and $R^{4'}$ are radicals selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals, provided that when R^1 or R^4 is isopropyl, R^2 or R^3 is not $ArCOCH_3$; X^{-} is a suitable charge-balancing counterion, preferably a bleach-compatible counterion; and v is an integer from 1 to 3.

Preferably, the oxaziridinium cations and polyions, which have a net charge of from about +3 to about -3, are represented by formula [XIII]:

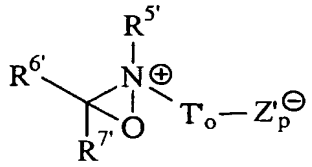


[XIII]

wherein m is 1 to 3 when G is present and m is 1 to 4 when G is not present; and n is an integer from 0 to 4; each $R^{20'}$ is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal $R^{20'}$ substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring, provided that when $R^{19'}$ is isopropyl, $R^{20'}$ is not $COCH_3$; $R^{18'}$ may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; $R^{19'}$ may be a substituted or unsubstituted, saturated or unsaturated, radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl and heterocyclic ring. G is selected from the group consisting of: (1) -O- ; (2) $-N(R^{23'})-$; and (3) $-N(R^{23'}R^{24'})-$; $R^{21'}$-$R^{24'}$ are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched C_1-C_{12} alkyls, alkylenes, alkoxys, aryls, alkaryls, aralkyls, cycloalkyls, and heterocyclic rings; provided that any of $R^{18'}$, $R^{19'}$, $R^{21'}$-$R^{24'}$ may be joined together with any other of $R^{18'}$, $R^{19'}$, $R^{21'}$-$R^{24'}$ to form part of a common ring; any geminal $R^{21'}$ - $R^{22'}$ may combine to form a carbonyl; any vicinal $R^{21'}$ - $R^{24'}$ may join to form unsaturation; and wherein any one group of substituents $R^{21'}$ - $R^{24'}$ may combine to form a substituted or unsubstituted fused unsaturated moiety; and wherein any one group of substituents $R^{21'}$ - $R^{24'}$ may combine to form a substituted or unsubstituted fused unsaturated moiety; X^- is a suitable charge-balancing counterion, preferably a bleach-compatible counterion.

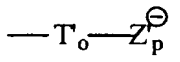
More preferred oxaziridinium cations and oxaziridinium polyions having a net charge of from about +3 to about -3, as represented by the formula [XIII], include those of formula [XIII] where $R^{18'}$ is H or methyl, and $R^{19'}$ is H or substituted or unsubstituted, saturated or unsaturated, C_1 - C_{14} alkyl or cycloalkyl.

b. Oxaziridinium Zwitterions - The oxaziridinium zwitterions, which have a net charge of from about +3 to about -3, are represented by formula [IV]:



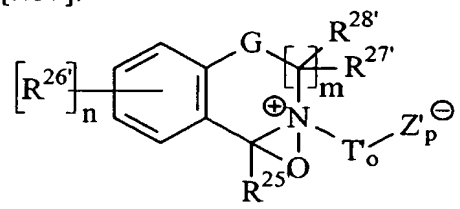
[IV]

where $R^{5'}$-$R^{7'}$ are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; also present in this formula is the radical represented by the formula:



where $Z'_p{}^-$ is covalently bonded to T'_o, and $Z'_p{}^-$ is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$ and p is either 1, 2 or 3; T'_o is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl, and heterocyclic ring.

Preferably, the oxaziridinium zwitterions having a net charge of from about +3 to about -3, and are represented by formula [XIV]:



[XIV]

wherein m is 1 to 3 when G is present and m is 1 to 4 when G is not present; and n is an integer from 0 to 4; each $R^{26'}$ is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring,

fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal $R^{26'}$ substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; $R^{25'}$ may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; the radical represented by the formula:

$$—T'_o—Z'^{\ominus}_p$$

where Z'_p^- is covalently bonded to T'_o, and Z'_p^- is selected from the group consisting of $-CO_2^-$, $-SO_3^-$, $-OSO_3^-$, $-SO_2^-$ and $-OSO_2^-$, and p is either 1 or 2; T'_o is selected from the group consisting of:

$$—(C)q—$$
(with $R^{29'}$ on each carbon)

wherein q is an integer from 1 to 8; $R^{29'}$ is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups, provided that all $R^{29'}$ groups are not independently selected to be H; G is selected from the group consisting of: (1) -O- ; (2) $-N(R^{30'})-$; and (3) $-N(R^{30'}R^{31'})-$; $R^{27'}$, $R^{28'}$, $R^{30'}$ and $R^{31'}$ are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of $R^{25'}$, $R^{26'}$, $R^{27'}$, $R^{28'}$, $R^{30'}$ and $R^{31'}$ may be joined together with any other of $R^{25'}$, $R^{26'}$, $R^{27'}$, $R^{28'}$, $R^{30'}$ and $R^{31'}$ to form part of a common ring; any geminal $R^{27'}$- $R^{28'}$ may combine to form a carbonyl; any vicinal $R^{27'}$- $R^{31'}$ may join to form unsaturation; and wherein any one group of substituents $R^{27'}$- $R^{31'}$ may combine to form a substituted or unsubstituted fused unsaturated moiety; and provided that the radical represented by the formula:

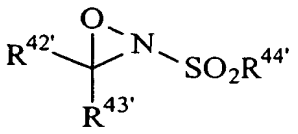
$$—T'_o—Z'^{\ominus}_p$$

is not $CH_2CH(OSO_3^-)R^{41}$ wherein R^{41} is selected from the group consisting of geminal dimethyl substituted alkyl, unsubstituted alkyl and phenyl.

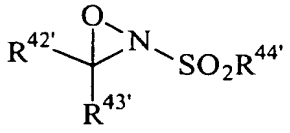
More preferred aryliminium zwitterions, which have a net charge of from about +3 to about -3, as represented by the formula [XIV], include those of formula [XIV] where $R^{25'}$ is H or methyl, and for the radical represented by the formula:

Z'_p^- is $-CO_2^-$, $-SO_3^-$ or $-OSO_3^-$, and p is 1 or 2.

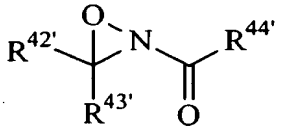
c) Oxaziridine Sulfonimines, Phosphonimines, N-Acylimines, Thiodiazole Dioxides - The oxaziridine sulfonimines [XXIVa], phosphonimines [XXIVb], N-acylimines [XXV] and thiodiazole dioxides [XXVI] and [XXVII] are represented as follows:



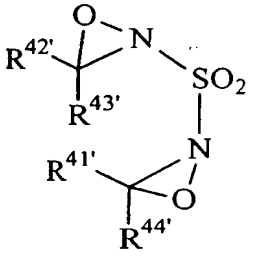
[XXIVa]



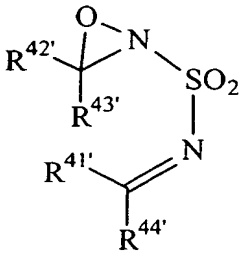
[XXIVb]



[XXV]



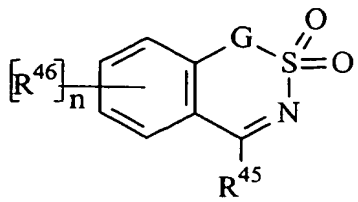
[XXVI]



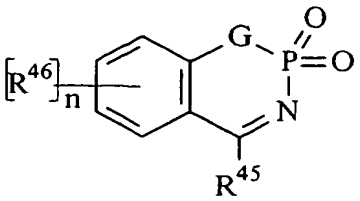
[XXVII]

where $R^{41'}$-$R^{44'}$, when present, are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, carboalkoxy radicals, provided that any of $R^{41'}$-$R^{44'}$ may be joined together with any other $R^{41'}$-$R^{44'}$ to form part of a common ring, including a fused aryl, fused carbocyclic or fused heterocyclic ring.

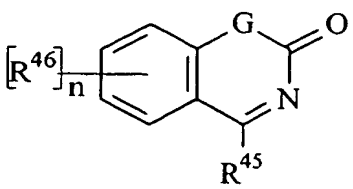
d) Sulfonimines [XXVIIIa], phosphonimines [XXVIIIb], N-acylimines [XXIX] are represented as follows:



[XXVIIIa]



[XXVIIIb]



[XXIX]

wherein each R^{46} is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R^{46} substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R^{45} may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; G, when present, is selected from the group consisting of: (1) -O- ; (2) -N(R^{47})-; and (3) -N($R^{47}R^{48}$)-; R^{47}-R^{48} are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched C_1-C_{12} alkyls, alkylenes, alkoxys, aryls, alkaryls, aralkyls, cycloalkyls, and heterocyclic rings.

Suitable examples of X^-, an anionic counterion, include, but are not limited to: BF_4^-, OTS^-, and other anionic counterions disclosed in WO 97/06147, WO 95/13352, WO 95/13353, WO 95/13351, WO 98/23717, U.S. Patent Nos. 5,360,568, 5,360569, 5,482,515, 5,550,256, 5,478,357, 5,370,826, 5,442,066, EP 728 182 B1 and UK 1 215 656. Preferably, the anionic counterions are bleach-compatible.

For any structures that carry no net charge, no counterions are associated with the compound.

For any structures that carry a net negative charge, suitable examples of X^+, a cationic counterion include, but are not limited to Na^+, K^+, H^+.

For any structures that carry a net multiple charge, suitable examples of anionic and cationic counterions include, but are not limited to those described above.

Other Organic Catalyst Compounds - In addition to the bleach boosters, bleaching species and modified amines and amine oxides disclosed above, organic catalyst compounds can be any compound known in the art that is capable of reacting with a peracid to form an oxygen transfer agent (a bleach).

Concentration of Organic Catalyst Compounds - The organic catalyst compounds of the present invention may be added to a wash solution in levels of from about 0.00001% (0.0001 ppm) to about 10% (100 ppm) by weight of the composition, and preferably from about 0.0001% (0.001

ppm) to about 2% (20 ppm) by weight of the composition, more preferably from about 0.005% (0.05 ppm) to about 0.5% (5 ppm), even more preferably from about 0.01% (0.1 ppm) to about 0.2% (2 ppm). Most preferably from about 0.02% (0.2 ppm) to about 0.1% (1 ppm).

Preferably, the bleaching compositions of the present invention bleach composition comprise an amount of organic catalyst compound such that the resulting concentration of the bleach boosting compound in a wash solution is from about 0.001 ppm to about 5 ppm.

Further, preferably the bleach compositions of the present invention comprise an amount of peroxygen compound, when present, and an amound of organic catalyst compound, such that the resulting molar ratio of said peroxygen compound to organic catalyst compound in a wash solution is preferably greater than 1:1, more preferably greater than 10:1, even more preferably greater than 50:1. The preferred molar ratio ranges of peroxygen compound to cationic organic catalyst compound range from about 30,000:1 to about 10:1, even more preferably from about 10,000:1 to about 50:1, yet even more preferably from about 5,000:1 to about 100:1, still even more preferably from about 3,500:1 to about 150:1.

The conversion values (in ppm) are provided for exemplary purposes, based on an in-use product concentration of 1000 ppm. A 1000 ppm wash solution of a product containing 0.2% organic catalyst compound by weight results in a organic catalyst compound concentration of 2 ppm. Similarly, a 3500 ppm wash solution of a product containing 0.2% organic catalyst compound by weight results in a organic catalyst compound concentration of 6.5 ppm.

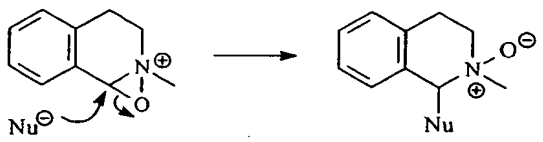
The method for delivering organic catalyst compounds of the present invention and the method for delivering bleaching compositions (products) containing such organic catalyst compounds that are particularly useful in the methods of the present invention are the organic catalyst compounds and compositions containing same that satisfy the preferred method for bleaching a stained substrate in an aqueous medium with a peroxygen source and with an organic catalyst compound whose structures is defined herein and wherein said medium contains active oxygen from the peroxygen compound from about 0.05 to about 250 ppm per liter of medium, and said organic catalyst compound from 0.001 ppm to about 5 ppm, preferably from about 0.01 ppm to about 3 ppm, more preferably from about 0.1 ppm to about 2 ppm, and most preferably from about 0.2 ppm to about 1 ppm.

Such a preferred method for bleaching a stained substrate in an aqueous medium with a peroxygen source and with an organic catalyst compound is of particular value for those applications in which the color safety of the stained substrate in need of cleaning is a concern. In such applications the preferred embodiment (e.g., 0.01 ppm to about 3 ppm) is of particular importance in terms of achieving acceptable fabric color safety. For other applications in which

color safety of the stained substrate in need of cleaning is of less concern, a higher in-use concentration may be preferred.

DECOMPOSITION OF ORGANIC CATALYSTS

The organic catalysts, specifically the bleach boosting compounds of the present invention are susceptible to decomposition by various decomposition pathways including, but not limited to, the aromatization pathway. The aromatization (decomposition) reaction of 6-membered ring boosters is well known in the art, as exemplified, without being limited by theory, in Hanquet et al., *Tetrahedron* **1993**, *49*, pp. 423-438. Other means of decomposition include, but are not limited to, attack on the bleach boosting compound and/or on the bleaching species by nucleophiles, including but not limited to attack by hydroxide anion, perhydroxide anion, carboxylate anion, percarboxylate anion and other nucleophiles present under in-wash conditions. For example, and without intending to be bound by theory, the decomposition reaction of a 6-membered ring oxaziridinium, the overall process of which can lead to reduced bleaching efficiency, is exemplified as set forth below:



METHODS FOR DELAYED (CONTROLLED) ADDITION OF ORGANIC CATALYST COMPOUNDS

It has surprisingly been found with organic catalyst compounds of limited lifetime, that the addition of organic catalyst compounds by a delivery means to a wash solution after a fabric has been added to a wash solution, especially a wash solution that contains a peroxygen source, provides enhanced bleaching compared to the addition of such organic catalyst compounds to the wash solution before a fabric has been added to the wash solution. It is believed, without being limited by theory, that the organic catalyst compound undergoes decomposition in the wash solution prior to the introduction of the fabric load. One method for improving the performance of organic catalyst compounds is to delay the addition of the organic catalyst compound of the present invention to the wash solution. Methods for delayed (controlled) addition of organic catalyst compounds are more fully described in copending and co-owned U.S. Provisional Patent Application entitled "Controlled Availability of Formulation Components, Compositions and Laundry Methods Employing Same" filed August 27, 1999 (P&G Attorney Docket Number 7749P).

Another method of improving the performance of organic catalyst compounds is to use an organic catalyst compound with increased stability to the wash conditions. This application describes organic catalyst compounds which exhibit an organic catalyst lifetime of from about 15 seconds to about 20 minutes as determined by Test Protocols I and/or II, described hereinafter.

BLEACHING COMPOSITIONS COMPRISING ORGANIC CATALYST COMPOUNDS

In addition to the use of organic catalyst compounds discussed above, the organic catalyst compounds of the present invention may be employed in conjunction with or without, preferably with a peroxygen source in other bleaching compositions, regardless of their form. For example, the organic catalyst compounds may be employed in a laundry additive product.

In the bleaching compositions of the present invention, the peroxygen source may be present in levels of from about 0.1% (1 ppm) to about 60% (600 ppm) by weight of the composition, and preferably from about 1% (10 ppm) to about 40% (400 ppm) by weight of the composition, and the organic catalyst compound may be present from about 0.00001% (0.0001 ppm) to about 10% (100 ppm) by weight of the composition, and preferably from about 0.0001% (0.001 ppm) to about 1% (10 ppm) by weight of the composition, more preferably from about 0.001% (0.01 ppm) to about 0.5% (5 ppm), even more preferably from about 0.004% (0.04 ppm) to about 0.25% (2.5 ppm). Most preferably from about 0.01% (0.1 ppm) to about 0.1% (1 ppm).

The organic catalyst compounds and bleaching compositions comprising the organic catalyst compounds of the present invention may be advantageously employed in laundry applications, hard surface cleaning, automatic dishwashing applications, whitening and/or bleaching applications associated with wood pulp and/or textiles, antimicrobial and/or disinfectant applications, as well as cosmetic applications such as dentures, teeth, hair and skin. However, due to the unique advantages of increased effectiveness in cold and possibly warm water solutions due to possible increased stability, the organic catalyst compounds of the present invention are ideally suited for laundry applications such as the bleaching of fabrics through the use of bleach-containing detergents or laundry bleach additives. Furthermore, the bleach boosting compounds of the present invention may be employed in granular, powder, bar, paste, foam, gel and liquid compositions.

Accordingly, the bleaching compositions of the present invention may include various additional ingredients which are desirable in laundry applications. Such ingredients include detersive surfactants, bleach catalysts, builders, chelating agents, enzymes, polymeric soil release agents, brighteners and various other ingredients. Compositions including any of these various additional ingredients preferably have a pH of about 6 to about 12, preferably from about 8 to about 10.5 in a 1% solution of the bleaching composition.

The bleaching compositions preferably include at least one detersive surfactant, at least one chelating agent, at least one detersive enzyme and preferably has a pH of about 6 to about 12, preferably from about 8 to about 10.5 in a 1% solution of the bleaching composition.

In another embodiment of the present invention, a method for laundering a fabric in need of laundering is provided. The preferred method comprises contacting the fabric with a laundry solution. The fabric may comprise most any fabric capable of being laundered in normal consumer use conditions. The laundry solution comprises a bleaching composition, as fully described herein. The water temperatures preferably range from about 0 °C to about 50 °C or higher. The water to fabric ratio is preferably from about 1:1 to about 15:1.

The laundry solution may further include at least one additional ingredient selected from the group consisting of detersive surfactants, chelating agents, detersive enzymes and mixtures thereof. Preferably, the laundry solution has a pH of about 6 to about 12, preferably from about 8 to about 10.5 in a 1% solution of the bleaching composition.

In accordance with another aspect of the present invention, a laundry additive product is provided. The laundry additive product comprises an organic catalyst compound, as fully described above. Such a laundry additive product would be ideally suited for inclusion in a wash process when additional bleaching effectiveness is desired. Such instances may include, but are not limited to, low-temperature and medium temperature solution laundry application.

It is desirable that the laundry additive product further includes a peroxygen source, as fully described above. The laundry additive product can also include powdered or liquid compositions containing a hydrogen peroxide source or a peroxygen source as fully defined above.

Furthermore, if the laundry additive product includes a hydrogen peroxide source, it is desirable that the laundry additive product further includes a bleach activator, as fully described above.

Preferably, the laundry additive product is packaged in dosage form for addition to a laundry process where a source of peroxygen is employed and increased bleaching effectiveness is desired. Such single dosage form may comprise a pill, tablet, gelcap or other single dosage unit such as pre-measured powders or liquids. A filler or carrier material may be included to increase the volume of composition if desired. Suitable filler or carrier materials may be selected from but not limited to various salts of sulfate, carbonate and silicate as well as talc, clay and the like. Filler or carrier materials for liquid compositions may be water or low molecular weight primary and secondary alcohols including polyols and diols. Examples include methanol, ethanol, propanol and isopropanol. Monohydric alcohols may also be employed. The compositions may contain from about 5% to about 90% of such materials. Acidic fillers can be used to reduce pH.

A preferred bleaching composition is a bleaching composition comprising:

(a) a peroxygen source; and

(b) an organic catalyst compounds;

wherein the organic catalyst compounds becomes active in a wash solution containing said bleaching composition a period of time after said peroxygen source becomes active. The peroxygen source, like discussed above, is preferably selected from the group consisting of:

(i) preformed peracid compounds selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof, and

(ii) hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

Bleaching System - In addition to the organic catalyst of the present invention, the bleaching compositions of the present invention preferably comprise a bleaching system. Bleaching systems typically comprise a peroxygen source. Peroxygen sources are well-known in the art and the peroxygen source employed in the present invention may comprise any of these well known sources, including peroxygen compounds as well as compounds which under consumer use conditions provide an effective amount of peroxygen in situ. The peroxygen source may include a hydrogen peroxide source, the in situ formation of a peracid anion through the reaction of a hydrogen peroxide source and a bleach activator, preformed peracid compounds or mixtures of suitable peroxygen sources. Of course, one of ordinary skill in the art will recognize that other sources of peroxygen may be employed without departing from the scope of the invention. Preferably, the peroxygen source is selected from the group consisting of:

(i) preformed peracid compounds selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof, and

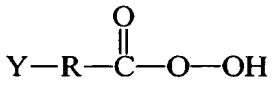
(ii) hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

When present, peroxygen sources (peracids and/or hydrogen peroxide sources) will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition. If present, the amount of bleach activator will typically

be from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the bleaching composition comprising the bleaching agent-plus-bleach activator.

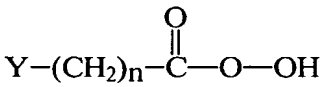
a. Preformed Peracids - The preformed peracid compound as used herein is any convenient compound which is stable and which under consumer use conditions provides an effective amount of peracid anion. The organic catalysts of the present invention may of course be used in conjunction with a preformed peracid compound selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof, examples of which are described in U.S. Patent No. 5,576,282 to Miracle et al.

One class of suitable organic peroxycarboxylic acids have the general formula:

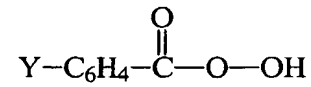


wherein R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y is hydrogen, halogen, alkyl, aryl, -C(O)OH or -C(O)OOH.

Organic peroxyacids suitable for use in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxycarboxylic acid is aliphatic, the unsubstituted peracid has the general formula:



where Y can be, for example, H, CH_3, CH_2Cl, C(O)OH, or C(O)OOH; and n is an integer from 0 to 20. When the organic peroxycarboxylic acid is aromatic, the unsubstituted peracid has the general formula:



wherein Y can be, for example, hydrogen, alkyl, alkylhalogen, halogen, C(O)OH or C(O)OOH.

Typical monoperoxy acids useful herein include alkyl and aryl peroxyacids such as:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acid, e.g. peroxy-a-naphthoic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), and *o*-carboxybenzamidoperoxyhexanoic acid (sodium salt);

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxylauric acid, peroxystearic acid, N-nonanoylaminoperoxycaproic acid (NAPCA), N,N-(3-octylsuccinoyl)aminoperoxycaproic acid (SAPA) and N,N-phthaloylaminoperoxycaproic acid (PAP);

(iii) amidoperoxyacids, e.g. mononononylamide of either peroxysuccinic acid (NAPSA) or of peroxyadipic acid (NAPAA).

Typical diperoxyacids useful herein include alkyl diperoxyacids and aryldiperoxyacids, such as:

(iv) 1,12-diperoxydodecanedioic acid;

(v) 1,9-diperoxyazelaic acid;

(vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vii) 2-decyldiperoxybutane-1,4-dioic acid;

(viii) 4,4'-sulfonylbisperoxybenzoic acid.

Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent 4,634,551 to Burns et al., European Patent Application 0,133,354, Banks et al. published February 20, 1985, and U.S. Patent 4,412,934, Chung et al. issued November 1, 1983. Sources also include 6-nonylamino-6-oxoperoxycaproic acid as fully described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al. Persulfate compounds such as for example OXONE, manufactured commercially by E.I. DuPont de Nemours of Wilmington, DE can also be employed as a suitable source of peroxymonosulfuric acid.

b. Hydrogen Peroxide Sources - The hydrogen peroxide source may be any suitable hydrogen peroxide source and present at such levels as fully described in U.S. Patent No. 5,576,282. For example, the hydrogen peroxide source may be selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof.

Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by

weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"). However, chlorine-type bleaches are less preferred for compositions which comprise enzymes.

b. Bleach Activators - Preferably, the peroxygen source in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about 1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. A bleach activator as used herein is any compound which when used in conjunction with a hydrogen peroxide source leads to the in situ production of the peracid corresponding to the bleach activator. Various non limiting examples of activators are fully disclosed in U.S. Patent No. 5,576,282, U.S. Patent 4,915,854 and U.S. Patent 4,412,934. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C_{10}-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonanoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, lauroyloxybenzenesulphonate (LOBS or C_{12}-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C_{11}-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11, 1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et

al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 08/064,564, all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

Quaternary substituted bleach activators may also be included. The present bleaching compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-octanamidocaproyl) oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido caproyl)oxybenzenesulfonate and mixtures thereof.

Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C_6H_4 ring to which is fused in the 1,2-positions a moiety --C(O)OC(R^1)=N-.

Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639 Willey et al., issued April 2, 1996 incorporated herein by reference).

d. Organic Peroxides, especially Diacyl Peroxides - In addition to the bleaching agents described above, the bleaching compositions of the present invention can optionally include organic peroxides. Organic peroxides are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages

63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

e. Metal-containing Bleach Catalysts - The bleaching compositions can also optionally include metal-containing bleach catalysts, preferably manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. 4,430,243 Bragg, issued February 2, 1982.

i. Manganese Metal Complexes - If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,576,282 Miracle et al., issued November 19, 1996; U.S. 5,246,621 Favre et al., issued September 21, 1993; U.S. 5,244,594 Favre et al., issued September 14, 1993; U.S. 5,194,416 Jureller et al., issued March 16, 1993; U.S. 5,114,606 van Vliet et al., issued May 19, 1992; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})\text{-}(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. 4,430,243 included by reference herein above and U.S. 5,114,611 van Kralingen, issued May 19, 1992. The use of manganese with various complex ligands to enhance bleaching is also reported in the following: U.S. 4,728,455 Rerek, issued March 1, 1988; U.S. 5,284,944 Madison, issued February 8, 1994; U.S. 5,246,612 van Dijk et al., issued September 21, 1993; U.S. 5,256,779 Kerschner et al., issued October 26, 2993; U.S. 5,280,117 Kerschner et al., issued January 18, 1994; U.S. 5,274,147 Kerschner et al., issued December 28, 1993; U.S. 5,153,161 Kerschner et al., issued October 6, 1992; and U.S. 5,227,084 Martens et al., issued July 13, 1993.

ii. Cobalt Metal Complexes - Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. 5,597,936 Perkins et al., issued January 28, 1997; U.S. 5,595,967 Miracle et al., January 21, 1997; U.S. 5,703,030 Perkins et al., issued December 30, 1997; and M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg.

Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]$ T_y, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. 5,597,936, U.S. 5,595,967, U.S. 5,703,030, cited herein above, the Tobe article and the references cited therein, and in U.S. Patent 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

iii. Transition Metal Complexes of Macropolycyclic Rigid Ligands - Compositions herein may also suitably include as bleach catalyst a transition metal complex of a macropolycyclic rigid ligand. The phrase "macropolycyclic rigid ligand" is sometimes abbreviated as "MRL" in discussion below. The amount used is a catalytically effective amount, suitably about 1 ppb or more, for example up to about 99.9%, more typically about 0.001 ppm or more, preferably from about 0.05 ppm to about 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

Suitable transition metals e.g., Mn are illustrated hereinafter. "Macropolycyclic" means a MRL is both a macrocycle and is polycyclic. "Polycyclic" means at least bicyclic. The term "rigid" as used herein herein includes "having a superstructure" and "cross-bridged". "Rigid" has been defined as the constrained converse of flexibility: see D.H. Busch., Chemical Reviews., (1993), 93, 847-860, incorporated by reference. More particularly, "rigid" as used herein means that the MRL must be determinably more rigid than a macrocycle ("parent macrocycle") which is otherwise identical (having the same ring size and type and number of atoms in the main ring) but lacking a superstructure (especially linking moieties or, preferably cross-bridging moieties) found in the MRL's. In determining the comparative rigidity of macrocycles with and without superstructures, the practitioner will use the free form (not the metal-bound form) of the macrocycles. Rigidity is well-known to be useful in comparing macrocycles; suitable tools for determining, measuring or comparing rigidity include computational methods (see, for example, Zimmer, Chemical Reviews, (1995), 95(38), 2629-2648 or Hancock et al., Inorganica Chimica Acta, (1989), 164, 73-84.

Preferred MRL's herein are a special type of ultra-rigid ligand which is cross-bridged. A "cross-bridge" is nonlimitingly illustrated in 1.11 hereinbelow. In 1.11, the cross-bridge is a –

CH_2CH_2- moiety. It bridges N^1 and N^8 in the illustrative structure. By comparison, a "same-side" bridge, for example if one were to be introduced across N^1 and N^{12} in 1.11, would not be sufficient to constitute a "cross-bridge" and accordingly would not be preferred.

Suitable metals in the rigid ligand complexes include Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV). Preferred transition-metals in the instant transition-metal bleach catalyst include manganese, iron and chromium.

More generally, the MRL's (and the corresponding transition-metal catalysts) herein suitably comprise:

(a) at least one macrocycle main ring comprising four or more heteroatoms; and

(b) a covalently connected non-metal superstructure capable of increasing the rigidity of the macrocycle, preferably selected from

(i) a bridging superstructure, such as a linking moiety;

(ii) a cross-bridging superstructure, such as a cross-bridging linking moiety; and

(iii) combinations thereof.

The term "superstructure" is used herein as defined in the literature by Busch et al., see, for example, articles by Busch in "Chemical Reviews".

Preferred superstructures herein not only enhance the rigidity of the parent macrocycle, but also favor folding of the macrocycle so that it coordinates to a metal in a cleft. Suitable superstructures can be remarkably simple, for example a linking moiety such as any of those illustrated in Fig. 1 and Fig. 2 below, can be used.

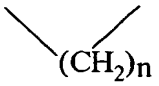


Fig. 1

wherein n is an integer, for example from 2 to 8, preferably less than 6, typically 2 to 4, or

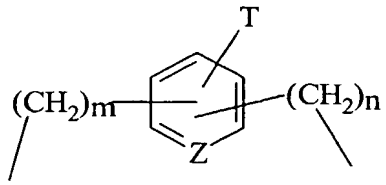


Fig. 2

wherein m and n are integers from about 1 to 8, more preferably from 1 to 3; Z is N or CH; and T is a compatible substituent, for example H, alkyl, trialkylammonium, halogen, nitro, sulfonate, or

the like. The aromatic ring in 1.10 can be replaced by a saturated ring, in which the atom in Z connecting into the ring can contain N, O, S or C.

Suitable MRL's are further nonlimitingly illustrated by the following compound:

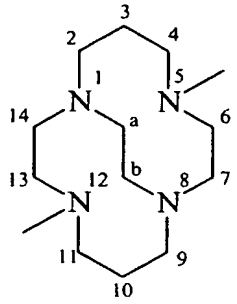


Fig. 3

This is a MRL in accordance with the invention which is a highly preferred, cross-bridged, methyl-substituted (all nitrogen atoms tertiary) derivative of cyclam. Formally, this ligand is named 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane using the extended von Baeyer system. See "A Guide to IUPAC Nomenclature of Organic Compounds: Recommendations 1993", R. Panico, W.H. Powell and J-C Richer (Eds.), Blackwell Scientific Publications, Boston, 1993; see especially section R-2.4.2.1.

Transition-metal bleach catalysts of Macrocyclic Rigid Ligands which are suitable for use in the invention compositions can in general include known compounds where they conform with the definition herein, as well as, more preferably, any of a large number of novel compounds expressly designed for the present laundry or cleaning uses, and non-limitingly illustrated by any of the following:

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Hexafluorophosphate

Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III) Hexafluorophosphate

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Tetrafluoroborate

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III) Hexafluorophosphate

Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II).

(f) Other Bleach Catalysts - The compositions herein may comprise one or more other bleach catalysts. Preferred bleach catalysts are zwitterionic bleach catalysts, which are described in U.S. Patent No. 5,576,282 (especially 3-(3,4-dihydroisoquinolinium) propane sulfonate. Other bleach catalysts include cationic bleach catalysts are described in U.S. Patent Nos. 5,360,569, 5,442,066, 5,478,357, 5,370,826, 5,482,515, 5,550,256, and WO 95/13351, WO 95/13352, and WO 95/13353.

As a practical matter, and not by way of limitation, the compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the cleaning compositions.

Preferably, the peroxygen source is selected from hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

Preferably, the bleach activator is selected from the group consisting of hydrophobic bleach activators as disclosed herein.

The purpose of such a bleaching composition is to mitigate unwanted decomposition of the organic catalyst, and to allow the peracid to achieve bleaching performance on a fabric in need of cleaning, such as a stained fabric, in a wash solution prior to the availability of the organic catalyst.

The period of time between the peracid becoming active in a wash solution and the organic catalyst compounds becoming active can be in the range of from about 1 second to about 24 hours. Alternatively, since the organic catalyst compounds are relatively stable in the wash solution, the peracid can become active in the wash solution after the organic catalyst compound becomes active or available.

The purpose of a delayed addition bleaching composition (which may or may not be used in conjunction with this invention) is to allow the peracid to achieve maximum bleaching performance on a fabric in need of cleaning, such as a stained fabric, in a wash solution prior to the introduction of the organic catalyst compound. In other words, a bleaching composition comprising a organic catalyst compound which becomes active in a wash solution after a fabric in

need of cleaning has been added to the wash solution. Alternatively, since the organic catalyst compounds can have increased stability, a bleaching composition comprising an organic catalyst compound which becomes active in a wash solution prior to a fabric in need of cleaning has been added to the wash solution may be used.

The bleaching compositions of the present invention also comprise, in addition to one or more organic catalysts, described hereinbefore, one or more cleaning adjunct materials, preferably compatible with the organic catalyst(s) and/or any enzymes present in the bleaching composition. The term "compatible", as used herein, means the bleaching composition materials do not reduce the bleaching activity of the organic catalyst and/or any enzymatic activity of any enzyme present in the bleaching composition to such an extent that the organic catalyst and/or enzyme is not effective as desired during normal use situations. The term "cleaning adjunct materials", as used herein, means any liquid, solid or gaseous material selected for the particular type of bleaching composition desired and the form of the product (e.g., liquid; granule; powder; bar; paste; spray; tablet; gel; foam composition), which materials are also preferably compatible with the protease enzyme(s) and bleaching agent(s) used in the composition. Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form.

The specific selection of cleaning adjunct materials are readily made by considering the surface, item or fabric to be cleaned, and the desired form of the composition for the cleaning conditions during use (e.g., through the wash detergent use). Examples of suitable cleaning adjunct materials include, but are not limited to, surfactants, builders, bleaches, bleach activators, bleach catalysts, other enzymes, enzyme stabilizing systems, chelants, optical brighteners, soil release polymers, dye transfer agents, dispersants, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, alkalinity sources, solubilizing agents, carriers, processing aids, pigments and pH control agents as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101. Specific bleaching composition materials are exemplified in detail hereinafter.

If the cleaning adjunct materials are not compatible with the protease variant(s) in the bleaching compositions, then suitable methods of keeping the cleaning adjunct materials and the protease variant(s) separate (not in contact with each other) until combination of the two components is appropriate can be used. Suitable methods can be any method known in the art, such as gelcaps, encapulation, tablets, physical separation, etc.

Such bleaching compositions include detergent compositions for cleaning hard surfaces, unlimited in form (e.g., liquid, granular, paste, foam, spray, etc.); detergent compositions for

cleaning fabrics, unlimited in form (e.g., granular, liquid, bar formulations, etc.); dishwashing compositions (unlimited in form and including both granular and liquid automatic dishwashing); oral bleaching compositions, unlimited in form (e.g., dentifrice, toothpaste and mouthwash formulations); and denture bleaching compositions, unlimited in form (e.g., liquid, tablet).

The fabric bleaching compositions of the present invention are mainly intended to be used in the wash cycle of a washing machine; however, other uses can be contemplated, such as pretreatment product for heavily-soiled fabrics, or soaking product; the use is not necessarily limited to the washing-machine context, and the compositions of the present invention can be used alone or in combination with compatible handwash compositions.

The bleaching compositions may include from about 1% to about 99.9% by weight of the composition of the cleaning adjunct materials.

As used herein, "non-fabric bleaching compositions" include hard surface bleaching compositions, dishwashing compositions, oral bleaching compositions, denture bleaching compositions and personal cleansing compositions.

When the bleaching compositions of the present invention are formulated as compositions suitable for use in a laundry machine washing method, the compositions of the present invention preferably contain both a surfactant and a builder compound and additionally one or more cleaning adjunct materials preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional cleaning adjunct materials.

The compositions of the present invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other cleaning adjunct materials selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litter, preferably 500 to 950 g/litter of composition measured at 20°C.

The "compact" form of the bleaching compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the

total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulfates and chlorides. A preferred filler salt is sodium sulfate.

Liquid bleaching compositions according to the present invention can also be in a "concentrated form", in such case, the liquid bleaching compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid bleaching composition is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the bleaching composition.

Cleaning Adjunct Materials

While not essential for the purposes of the present invention, several conventional adjuncts illustrated hereinafter are suitable for use in the instant bleaching compositions and may be desirably incorporated in preferred embodiments of the invention, for example to assist or enhance cleaning performance, for treatment of the substrate to be cleaned, or to modify the aesthetics of the bleaching composition as is the case with perfumes, colorants, dyes or the like. The precise nature of these additional components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of the cleaning operation for which it is to be used. Unless otherwise indicated, the bleaching compositions of the invention may for example, be formulated as granular or powder-form all-purpose or "heavy-duty" washing agents, especially laundry detergents; liquid, gel or paste-form all-purpose washing agents, especially the so-called heavy-duty liquid types; liquid fine-fabric detergents; hand dishwashing agents or light duty dishwashing agents, especially those of the high-foaming type; machine dishwashing agents, including the various tablet, granular, liquid and rinse-aid types for household and institutional use; liquid cleaning and disinfecting agents, including antibacterial hand-wash types, laundry bars, mouthwashes, denture cleaners, car or carpet shampoos, bathroom cleaners; hair shampoos and hair-rinses; shower gels and foam baths and metal cleaners; as well as cleaning auxiliaries such as bleach additives and "stain-stick" or pre-treat types.

Surfactants - The compositions of the present invention preferably contain a detersive surfactant. The detersive surfactant is typically selected from the group consisting of anionic, nonionics, cationics, ampholytics, zwitterionics, and mixtures thereof. By selecting the type and amount of detersive surfactant, along with other adjunct ingredients disclosed herein, the present detergent compositions can be formulated to be used in the context of laundry cleaning or in other different cleaning applications, particularly including dishwashing. The particular surfactants

used can therefore vary widely depending upon the particular end-use envisioned. Suitable surfactants are described below. Examples of suitable nonionic, anionic, cationic amphoteric and zwitterionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

The surfactant is typically present at a level of from about 0.1%, preferably about 1%, more preferably about 5% by weight of the bleaching compositions to about 99.9%, preferably about 80%, more preferably about 35%, most preferably 30% about by weight of the bleaching compositions.

Anionic Surfactants - Anionic surfactants useful in the present invention are preferably selected from the group consisting of, linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxylated sulfates, sarcosinates, taurinates, and mixtures thereof. An effective amount, typically from about 0.5% to about 90%, preferably about 5% to about 60%, more preferably from about 10 to about 30%, by weight of anionic detersive surfactant can be used in the present invention.

Alkyl sulfate surfactants are another type of anionic surfactant of importance for use herein. In addition to providing excellent overall cleaning ability when used in combination with polyhydroxy fatty acid amides (see below), including good grease/oil cleaning over a wide range of temperatures, wash concentrations, and wash times, dissolution of alkyl sulfates can be obtained, as well as improved formulability in liquid detergent formulations are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali (Group IA) metal cation (e.g., sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of C_{12-16} are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl alkoxylated sulfate surfactants are another category of useful anionic surfactant. These surfactants are water soluble salts or acids typically of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A

is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium. Surfactants for use herein can be made from natural or synthetic alcohol feedstocks. Chain lengths represent average hydrocarbon distributions, including branching.

Additionally and preferably, the surfactant may be a midchain branched alkyl sulfate, midchain branched alkyl alkoxylate, or midchain branched alkyl alkoxylate sulfate. These surfactants are further described in No. 60/061,971, Attorney docket No 6881P October 14, 1997, No. 60/061,975, Attorney docket No 6882P October 14, 1997, No. 60/062,086, Attorney docket No 6883P October 14, 1997, No. 60/061,916, Attorney docket No 6884P October 14, 1997, No. 60/061,970, Attorney docket No 6885P October 14, 1997, No. 60/062,407, Attorney docket No 6886P October 14, 1997,. Other suitable mid-chain branched surfactants can be found in U.S. Patent applications Serial Nos. 60/032,035 (Docket No. 6401P), 60/031,845 (Docket No. 6402P), 60/031,916 (Docket No. 6403P), 60/031,917 (Docket No. 6404P), 60/031,761 (Docket No. 6405P), 60/031,762 (Docket No. 6406P) and 60/031,844 (Docket No. 6409P). Mixtures of these branched surfactants with conventional linear surfactants are also suitable for use in the present compositions.

Another preferred anionic surfactant are the so-called modified alkyl benzene sulfonate surfactants, or MLAS. Some suitable MLAS surfactants, methods of making them and exemplary compositions are further described in copending U.S. Patent applications Serial Nos. 60/053,319 (Docket No. 6766P), 60/053,318 (Docket No. 6767P), 60/053,321 (Docket No. 6768P), 60/053,209 (Docket No. 6769P), 60/053,328 (Docket No. 6770P), 60/053,186 (Docket No. 6771P), 60/055,437 (Docket No. 6796P), 60/105,017 (Docket No. 7303P), and 60/104,962 (Docket No. 7304P).

Examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants include: amine oxides, alkyl ethoxylate, alkanoyl glucose amide, alkyl betaines, sulfobetaine and mixtures thereof.

Amine oxides are semi-polar nonionic surfactants and include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

$$R^3(OR^4)_xN(R^5)_2 \rightarrow O$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides. Preferably the amine oxide is present in the composition in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%,by weight.

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic

surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

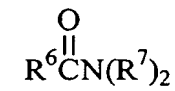
The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C_{11}-C_{15} linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:



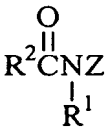
wherein R^6 is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C^2H_4O)_xH$ where x varies from about 1 to about 3.

Preferred amides are C_8-C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Preferably the nonionic surfactant, when present in the composition, is present in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%,by weight.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain an effective amount of polyhydroxy fatty acid amide surfactant. By "effective amount" is meant that the formulator of the composition can select an amount of polyhydroxy fatty acid amide to be incorporated into the compositions that will improve the cleaning performance of the detergent composition. In general, for conventional levels, the incorporation of about 1%, by weight, polyhydroxy fatty acid amide will enhance cleaning performance.

The detergent compositions herein will typically comprise about 1% weight basis, polyhydroxy fatty acid amide surfactant, preferably from about 3% to about 30%, of the polyhydroxy fatty acid amide. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5-C_{31} hydrocarbyl, preferably straight chain C_7-C_{19} alkyl or alkenyl, more preferably straight chain C_9-C_{17} alkyl or alkenyl, most preferably straight chain C_{11}-C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other

suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

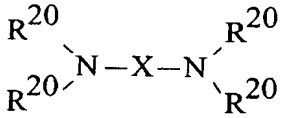
R^2-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

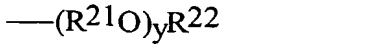
Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

Diamines - The preferred liquid detergent compositions, such as light duty liquid, LDL compositions, useful in the methods of the present invention may further comprise one or more diamines, preferably an amount of diamine such that the ratio of anionic surfactant present to the diamine is from about 40 : 1 to about 2: 1. Said diamines provide for increased removal of grease and greasy food material while maintaining suitable levels of suds.

The diamines suitable for use in the compositions of the present invention have the formula:



wherein each R^{20} is independently selected from the group consisting of hydrogen, C_1-C_4 linear or branched alkyl, alkyleneoxy having the formula:



wherein R^{21} is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^{22} is hydrogen, C_1-C_4 alkyl, and mixtures thereof; y is from 1 to about 10; X is a unit selected from:

i) C_3-C_{10} linear alkylene, C_3-C_{10} branched alkylene, C_3-C_{10} cyclic alkylene, C_3-C_{10} branched cyclic alkylene, an alkyleneoxyalkylene having the formula:

$$—(R^{21}O)_yR^{21}—$$

wherein R^{21} and y are the same as defined herein above;

ii) C_3-C_{10} linear, C_3-C_{10} branched linear, C_3-C_{10} cyclic, C_3-C_{10} branched cyclic alkylene, C_6-C_{10} arylene, wherein said unit comprises one or more electron donating or electron withdrawing moieties which provide said diamine with a pK_a greater than about 8; and

iii) mixtures of (i) and (ii)

provided said diamine has a pK_a of at least about 8.

The preferred diamines of the present invention have a pK_1 and pK_2 which are each in the range of from about 8 to about 11.5, preferably in the range of from about 8.4 to about 11, more preferably from about 8.6 to about 10.75. For the purposes of the present invention the term "pK_a" stands equally well for the terms "pK_1" and "pK_2" either separately or collectively. The term pK_a as used herein throughout the present specification in the same manner as used by those of ordinary skill in the art. pK_a values are readily obtained from standard literature sources, for example, "Critical Stability Constants: Volume 2, Amines" by Smith and Martel, Plenum Press, N.Y. and London, (1975).

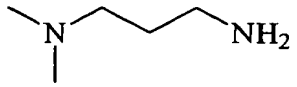
As an applied definition herein, the pK_a values of the diamines are specified as being measured in an aqueous solution at 25° C having an ionic strength of from about 0.1 to about 0.5 M. As used herein, the pK_a is an equilibrium constant dependent upon temperature and ionic strength, therefore, value reported by literature references, not measured in the above described manner, may not be within full agreement with the values and ranges which comprise the present invention. To eliminate ambiguity, the relevant conditions and/or references used for pK_a's of this invention are as defined herein or in "Critical Stability Constants: Volume 2, Amines". One typical method of measurement is the potentiometric titration of the acid with sodium hydroxide and determination of the pK_a by suitable methods as described and referenced in "The Chemist's Ready Reference Handbook" by Shugar and Dean, McGraw Hill, NY, 1990.

Preferred diamines for performance and supply considerations are 1,3-bis(methylamino)cyclohexane, 1,3-diaminopropane (pK_1=10.5; pK_2=8.8), 1,6-diaminohexane (pK_1=11; pK_2=10), 1,3-diaminopentane (Dytek EP) (pK_1=10.5; pK_2=8.9), 2-methyl 1,5-diaminopentane (Dytek A) (pK_1=11.2; pK_2=10.0). Other preferred materials are the

primary/primary diamines having alkylene spacers ranging from C_4-C_8. In general, primary diamines are preferred over secondary and tertiary diamines.

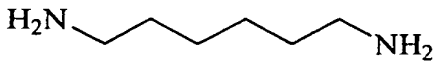
The following are non-limiting examples of diamines suitable for use in the present invention.

1-N,N-dimethylamino-3-aminopropane having the formula:



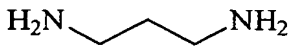
,

1,6-diaminohexane having the formula:



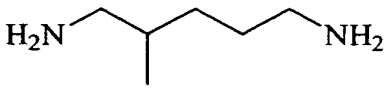
,

1,3-diaminopropane having the formula:



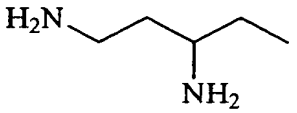
,

2-methyl-1,5-diaminopentane having the formula:



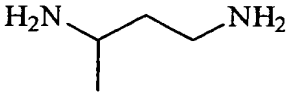
,

1,3-diaminopentane, available under the tradename Dytek EP, having the formula:



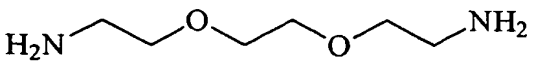
,

1,3-diaminobutane having the formula:



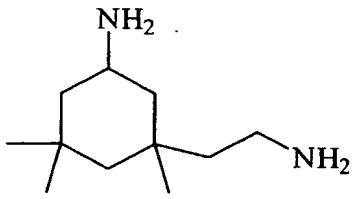
,

Jeffamine EDR 148, a diamine having an alkyleneoxy backbone, having the formula:



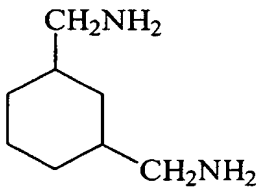
,

3-methyl-3-aminoethyl-5-dimethyl-1-aminocyclohexane (isophorone diamine) having the formula:



, and

1,3-bis(methylamino)cyclohexane having the formula:



ADDITIONAL DETERGENT COMPONENTS

The following are non-limiting examples of additional detergent components (adjunct ingredients) useful in the bleaching compositions, especially laundry detergent compositions, of the present invention, said adjunct ingredients include builders, optical brighteners, soil release polymers, dye transfer agents, dispersants, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

Builders - The bleaching compositions of the present invention preferably comprise one or more detergent builders or builder systems. When present, the compositions will typically comprise at least about 1% builder, preferably from about 5%, more preferably from about 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight, of detergent builder.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the

tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839 Rieck, issued May 12, 1987. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1}\cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$[M_z(zAlO_2)_y]\cdot xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669, Krummel et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the

designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in U.S. 3,128,287 Berg, issued April 7, 1964, U.S. 3,635,830 Lamberti et al., issued January 18, 1972, and U.S. 3,936,448 Lamberti, issued February 3, 1976. See also "TMS/TDS" builders of U.S. 4,663,071 Bush et al., issued May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679 Rapko, issued December 2, 1975; U.S. 4,158,635 Crutchfield et al., issued June 19, 1979; U.S. 4,120,874 Crutchfield et al., issued October 17, 1978; and U.S. 4,102,903 Crutchfield et al., issued July 25, 1978.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the bleaching compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush,

issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al., issued March 13, 1979 and in U.S. 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Chelating Agents - The bleaching compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Examples of suitable chelating agents and levels of use are described in U.S. Pat. Nos. 5,576,282 and 5,728,671.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% by weight of the bleaching compositions herein to about 15%, more preferably 3.0% by weight of the bleaching compositions herein.

Dye Transfer Inhibiting Agents - The bleaching compositions of the present invention may also include one or more compounds, dye transfer inhibiting agents, for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering and conditioning operations involving colored fabrics.

Suitable polymeric dye transfer inhibiting agents include, but are not limited to, polyvinylpyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof. Examples of such dye transfer inhibiting agents are disclosed in U.S. Pat. Nos. 5,707,950 and 5,707,951.

Additional suitable dye transfer inhibiting agents include, but are not limited to, cross-linked polymers. Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups on the backbone or on branches. Cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure.

In another embodiment, the cross-linked polymers entrap dyes by swelling.

Suitable cross-linked polymers are described in the co-pending European patent application 94870213.9.

Addition of such polymers also enhances the performance of the enzymes within the bleaching compositions herein.

The dye transfer inhibiting agents have the ability to complex or adsorb fugitive dyes wash out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

When present in the bleaching compositions herein, the dye transfer inhibiting agents are present at levels from about 0.0001%, more preferably about 0.01%, most preferably about 0.05% by weight of the bleaching compositions to about 10%, more preferably about 2%, most preferably about 1% by weight of the bleaching compositions.

Dispersants - The bleaching compositions of the present invention can also contain dispersants. Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts,

in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the detergent compositions of the present invention.

The compositions of the invention may contain a lime soap peptiser compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm $CaCo_3$ (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C_{16}-C_{18} dimethyl amine oxide, C_{12}-C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12}-C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C_{14}-C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene

sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Enzymes - The bleaching compositions can comprise in addition to the amylase of the present invention one or more detergent enzymes which provide cleaning performance and/or fabric care benefits. Such enzymes can include proteases, amylases, cellulases and lipases. Such materials are known in the art and are commercially available under such trademarks as . They may be incorporated into the non-aqueous liquid bleaching compositions herein in the form of suspensions, "marumes" or "prills". Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants, e.g., the enzymes marketed by Novo Nordisk under the tradename "SL" or the microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP." Suitable enzymes and levels of use are described in U.S. Pat. No. 5,576,282.

Enzymes added to the compositions herein in the form of conventional enzyme prills are especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the non-aqueous liquid phase of the composition. Prills in the compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus, compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, known amylases, mannanases, xyloglucanases and mixtures thereof. A preferred combination is a bleaching composition having a cocktail of conventional applicable enzymes like protease, lipase, cutinase and/or cellulase in conjunction with the amylase of the present invention.

Examples of such suitable enzymes are disclosed in U.S. Patent Nos. 5,576,282, 5,728,671 and 5,707,950

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and

MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. More preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, the protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO91/06637 and protease BLAP® described in WO91/02792. The proteolytic enzymes are incorporated in the bleaching compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Other particularly useful proteases are multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT Published Application Nos. WO 99/20727, WO 99/20726, and WO 99/20723 all owned by The Procter & Gamble Company.

More preferably the protease variant includes a substitution set selected from the group consisting of:

12/76/103/104/130/222/245/261;
62/103/104/159/232/236/245/248/252;
62/103/104/159/213/232/236/245/248/252;
62/101/103/104/159/212/213/232/236/245/248/252;
68/103/104/159/232/236/245;
68/103/104/159/230/232/236/245;
68/103/104/159/209/232/236/245;
68/103/104/159/232/236/245/257;
68/76/103/104/159/213/232/236/245/260;
68/103/104/159/213/232/236/245/248/252;

68/103/104/159/183/232/236/245/248/252;
68/103/104/159/185/232/236/245/248/252;
68/103/104/159/185/210/232/236/245/248/252;
68/103/104/159/210/232/236/245/248/252;
68/103/104/159/213/232/236/245;
98/103/104/159/232/236/245/248/252;
98/102/103/104/159/212/232/236/245/248/252;
101/103/104/159/232/236/245/248/252;
102/103/104/159/232/236/245/248/252;
103/104/159/230/236/245;
103/104/159/232/236/245/248/252;
103/104/159/217/232/236/245/248/252;
103/104/130/159/232/236/245/248/252;
103/104/131/159/232/236/245/248/252;
103/104/159/213/232/236/245/248/252; and
103/104/159/232/236/245.

Still even more preferably the protease variant includes a substitution set selected from the group consisting of:

12R/76D/103A/104T/130T/222S/245R/261D;
62D/103A/104I/159D/232V/236H/245R/248D/252K;
62D/103A/104I/159D/213R/232V/236H/245R/248D/252K;
68A/103A/104I/159D/209W/232V/236H/245R;
68A/76D/103A/104I/159D/213R/232V/236H/245R/260A;
68A/103A/104I/159D/213E/232V/236H/245R/248D/252K;
68A/103A/104I/159D/183D/232V/236H/245R/248D/252K;
68A/103A/104I/159D/232V/236H/245R;
68A/103A/104I/159D/230V/232V/236H/245R;
68A/103A/104I/159D/232V/236H/245R/257V;
68A/103A/104I/159D/213G/232V/236H/245R/248D/252K;
68A/103A/104I/159D/185D/232V/236H/245R/248D/252K;
68A/103A/104I/159D/185D/210L/232V/236H/245R/248D/252K;
68A/103A/104I/159D/210L/232V/236H/245R/248D/252K;
68A/103A/104I/159D/213G/232V/236H/245R;

98L/103A/104I/159D/232V/236H/245R/248D/252K;
98L/102A/103A/104I/159D/212G/232V/236H/245R/248D/252K;
101G/103A/104I/159D/232V/236H/245R/248D/252K;
102A/103A/104I/159D/232V/236H/245R/248D/252K;
103A/104I/159D/230V/236H/245R;
103A/104I/159D/232V/236H/245R/248D/252K;
103A/104I/159D/217E/232V/236H/245R/248D/252K;
103A/104I/130G/159D/232V/236H/245R/248D/252K;
103A/104I/131V/159D/232V/236H/245R/248D/252K;
103A/104I/159D/213R/232V/236H/245R/248D/252K; and
103A/104I/159D/232V/236H/245R.

Most preferably the protease variant includes the substitution set 101/103/104/159/232/236/245/248/252, preferably 101G/103A/104I/159D/232V/236H/245R/248D/252K.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.

Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing bleaching compositions are disclosed, for example, in U.S. Patent Nos. 5,576,282, 5,728,671 and 5,707,950, PCT International Applications WO 89/099813, WO89/09813 and in

European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substituted phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the bleaching composition at levels from 0.0001% to 2% of active enzyme by weight of the bleaching composition.

Other preferred enzymes that can be included in the bleaching compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 LIPASE® and LIPOMAX® (Gist-Brocades) and LIPOLASE® and LIPOLASE ULTRA®(Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to bleaching compositions have been described in e.g. WO 88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the bleaching composition at levels from 0.0001% to 2% of active enzyme by weight of the bleaching composition.

Known amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO 94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO94/18314, Genencor, published August 18, 1994 and WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in bleaching compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. 5,003,257; EP 252,666; WO 91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent Specification No. 1,296,839 (Novo). Other

suitable amylase are stability-enhanced amylases including PURAFACT OX AM® described in WO 94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95.

Examples of commercial α-amylases products are TERMAMYL®, BAN®, FUNGAMYL® and DURAMYL®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterized by having a specific activity at least 25% higher than the specific activity of TERMAMYL® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The compositions of the present invention may also comprise a mannanase enzyme. Preferably, the mannanase is selected from the group consisting of: three mannans-degrading enzymes : EC 3.2.1.25 : β-mannosidase, EC 3.2.1.78 : Endo-1,4-β-mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4-β-mannobiosidase and mixtures thereof. (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press).

More preferably, the treating compositions of the present invention, when a mannanase is present, comprise a β-1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and endo-1,4-mannanase and catalysing the reaction: random hydrolysis of 1,4-beta-D- mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving polyose chains containing mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of β-1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating β-1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with α-1,6 linked galactose sidebranches. These compounds may be acetylated.

The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans, glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetylesterases. The

oligomers which are released from the mannanases or by a combination of mannanases and α-galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by β-mannosidase and/or β-glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and an optimum pH of 5.5-7.5. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity at pH 5.0 and 55C and a pI of 4.8. JP-03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an alkaline, thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which may be useful for degradation or modification of plant or algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reseei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more preferably, a mannanase originating from a bacterial source. Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the mannanase from the strain *Bacillus agaradhaerens* NICMB 40482; the mannanase from *Bacillus subtilis* strain 168, gene yght; the mannanase from *Bacillus sp.* I633 and/or the mannanase from *Bacillus sp.* AAI12. Most preferred mannanase for the inclusion in the detergent compositions of the present invention is the mannanase enzyme originating from *Bacillus sp.* I633 as described in the co-pending Danish patent application No. PA 1998 01340.

The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5.

The alkaline mannanase from *Bacillus agaradhaerens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 32-343 of SEQ ID NO:2 as shown in U.S. patent application serial No. 09/111,256; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 97 to nucleotide 1029 as shown in U.S. patent application serial No. 09/111,256;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 32 to amino acid residue 343 as shown in U.S. patent application serial No. 09/111,256;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pSJ1678 comprising the polynucleotide molecule (the DNA sequence) encoding said mannanase has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 18 May 1998 under the deposition number DSM 12180.

A second more preferred enzyme is the mannanase from the *Bacillus subtilis* strain 168, which is described in the co-pending U.S. patent application serial No. 09/095,163. More specifically, this mannanase is:

i) is encoded by the coding part of the DNA sequence shown in SED ID No. 5 shown in the U.S. patent application serial No. 09/095,163 or an analogue of said sequence; and/or

ii) a polypeptide comprising an amino acid sequence as shown SEQ ID NO:6 shown in the U.S. patent application serial No. 09/095,163; or

iii) an analogue of the polypeptide defined in ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed in the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO:5 as shown in the U.S. patent application serial No. 09/095,163

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 6 as shown in the U.S. patent application serial No. 09/095,163;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

A third more preferred mannanase is described in the co-pending Danish patent application No. PA 1998 01340. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* I633;

ii) a polypeptide comprising an amino acid sequence as shown in positions 33-340 of SEQ ID NO:2 as shown in the Danish application No. PA 1998 01340; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 317 to nucleotide 1243 the Danish application No. PA 1998 01340;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 33 to amino acid residue 340 the Danish application No. PA 1998 01340;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM3 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 29 May 1998 under the deposition number DSM 12197.

A fourth more preferred mannanase is described in the Danish co-pending patent application No. PA 1998 01341. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* AAI 12;

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-362 of SEQ ID NO:2as shown in the Danish application No. PA 1998 01341; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 225 to nucleotide 1236 as shown in the Danish application No. PA 1998 01341;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 25 to amino acid residue 362 as shown in the Danish application No. PA 1998 01341;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM1 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 7 October 1998 under the deposition number DSM 12433.

The mannanase, when present, is incorporated into the treating compositions of the present invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The compositions of the present invention may also comprise a xyloglucanase enzyme. Suitable xyloglucanases for the purpose of the present invention are enzymes exhibiting endoglucanase activity specific for xyloglucan, preferably at a level of from about 0.001% to about 1%, more preferably from about 0.01% to about 0.5%, by weight of the composition. As used herein, the term "endoglucanase activity" means the capability of the enzyme to hydrolyze 1,4-β-D-glycosidic linkages present in any cellulosic material, such as cellulose, cellulose derivatives, lichenin, β-D-glucan, or xyloglucan. The endoglucanase activity may be determined in accordance with methods known in the art, examples of which are described in WO 94/14953 and hereinafter. One unit of endoglucanase activity (e.g. CMCU, AVIU, XGU or BGU) is defined as the production of 1 μmol reducing sugar/min from a glucan substrate, the glucan substrate being, e.g., CMC (CMCU), acid swollen Avicell (AVIU), xyloglucan (XGU) or cereal β -glucan (BGU). The reducing sugars are determined as described in WO 94/14953 and hereinafter. The specific activity of an endoglucanase towards a substrate is defined as units/mg of protein.

Suitable are enzymes exhibiting as its highest activity XGU endoglucanase activity (hereinafter "specific for xyloglucan"), which enzyme:

i) is encoded by a DNA sequence comprising or included in at least one of the following partial sequences

(a) ATTCATTTGT GGACAGTGGA C (SEQ ID No: 1)

(b) GTTGATCGCA CATTGAACCA (SEQ ID NO: 2)

(c) ACCCCAGCCG ACCGATTGTC (SEQ ID NO: 3)

(d) CTTCCTTACC TCACCATCAT (SEQ ID NO: 4)

(e) TTAACATCTT TTCACCATGA (SEQ ID NO: 5)

(f) AGCTTTCCCT TCTCTCCCTT (SEQ ID NO: 6)

(g) GCCACCCTGG CTTCCGCTGC CAGCCTCC (SEQ ID NO: 7)
(h) GACAGTAGCA ATCCAGCATT (SEQ ID NO: 8)
(i) AGCATCAGCC GCTTTGTACA (SEQ ID NO: 9)
(j) CCATGAAGTT CACCGTATTG (SEQ ID NO: 10)
(k) GCACTGCTTC TCTCCCAGGT (SEQ ID NO: 11)
(l) GTGGGCGGCC CCTCAGGCAA (SEQ ID NO: 12)
(m) ACGCTCCTCC AATTTTCTCT (SEQ ID NO: 13)
(n) GGCTGGTAG TAATGAGTCT (SEQ ID NO: 14)
(o) GGCGCAGAGT TTGGCCAGGC (SEQ ID NO: 15)
(p) CAACATCCCC GGTGTTCTGG G (SEQ ID NO: 16)
(q) AAAGATTCAT TTGTGGACAG TGGACGTTGA TCGCACATTG AACCAACCCC AGCCGACCGA
TTGTCCTTCC TTACCTCACC ATCATTTAAC ATCTTTTCAC CATGAAGCTT TCCCTTCTCT
CCCTTGCCAC CCTGGCTTCC GCTGCCAGCC TCCAGCGCCG CACACTTCTG CGGTCAGTGG
GATACCGCCA CCGCCGGTGA CTTCACCCTG TACAACGACC TTTGGGGCGA GACGGCCGGC
ACCGGCTCCC AGTGCACTGG AGTCGACTCC TACAGCGGCG ACACCATCGC TTGTCACACC
AGCAGGTCCT GGTCGGAGTA GCAGCAGCGT CAAGAGCTAT GCCAACG (SEQ ID NO:17) or
(r) CAGCATCTCC ATTGAGTAAT CACGTTGGTG TTCGGTGGCC CGCCGTGTTG CGTGGCGGAG
GCTGCCGGGA GACGGGTGGG GATGGTGGTG GGAGAGAATG TAGGGCGCCG TGTTTCAGTC
CCTAGGCAGG ATACCGGAAA ACCGTGTGGT AGGAGGTTTA TAGGTTTCCA GGAGACGCTG
TATAGGGGAT AAATGAGATT GAATGGTGGC CACACTCAAA CCAACCAGGT CCTGTACATA
CAATGCATAT ACCAATTATA CCTACCAAAA AAAAAAAAAA AAAAAAAAAA AAAA (SEQ ID NO:18)

or a sequence homologous thereto encoding a polypeptide specific for xyloglucan with endoglucanase activity,

ii) is immunologically reactive with an antibody raised against a highly purified endoglucanase encoded by the DNA sequence defined in i) and derived from *Aspergillus aculeatus*, CBS 101.43, and is specific for xyloglucan.

More specifically, as used herein the term "specific for xyloglucan" means that the endoglucanse enzyme exhibits its highest endoglucanase activity on a xyloglucan substrate, and preferably less than 75% activity, more preferably less than 50% activity, most preferably less than about 25% activity, on other cellulose-containing substrates such as carboxymethyl cellulose, cellulose, or other glucans.

Preferably, the specificity of an endoglucanase towards xyloglucan is further defined as a relative activity determined as the release of reducing sugars at optimal conditions obtained by incubation of the enzyme with xyloglucan and the other substrate to be tested, respectively. For instance, the specificity may be defined as the xyloglucan to β-glucan activity (XGU/BGU), xyloglucan to carboxy methyl cellulose activity (XGU/CMCU), or xyloglucan to acid swollen Avicell activity (XGU/AVIU), which is preferably greater than about 50, such as 75, 90 or 100.

The term "derived from" as used herein refers not only to an endoglucanase produced by strain CBS 101.43, but also an endoglucanase encoded by a DNA sequence isolated from strain CBS 101.43 and produced in a host organism transformed with said DNA sequence. The term "homologue" as used herein indicates a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for an endoglucanase enzyme specific for xyloglucan under certain specified conditions (such as presoaking in 5xSSC and prehybridizing for 1 h at -40°C in a solution of 5xSSC, 5xDenhardt's solution, and 50 μg of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 50 μCi 32-P-dCTP labeled probe for 18 h at -40°C and washing three times in 2xSSC, 0.2% SDS at 40°C for 30 minutes). More specifically, the term is intended to refer to a DNA sequence which is at least 70% homologous to any of the sequences shown above encoding an endoglucanase specific for xyloglucan, including at least 75%, at least 80%, at least 85%, at least 90% or even at least 95% with any of the sequences shown above. The term is intended to include modifications of any of the DNA sequences shown above, such as nucleotide substitutions which do not give rise to another amino acid sequence of the polypeptide encoded by the sequence, but which correspond to the codon usage of the host organism into which a DNA construct comprising any of the DNA sequences is introduced or nucleotide substitutions which do give rise to a different amino acid sequence and therefore, possibly, a different amino acid sequence and therefore, possibly, a different protein structure which might give rise to an endoglucanase mutant with different properties than the native enzyme. Other examples of possible modifications are insertion of one

or more nucleotides into the sequence, addition of one or more nucleotides at either end of the sequence, or deletion of one or more nucleotides at either end or within the sequence.

Endoglucanase specific for xyloglucan useful in the present invention preferably is one which has a XGU/BGU, XGU/CMU and/or XGU/AVIU ratio (as defined above) of more than 50, such as 75, 90 or 100.

Furthermore, the endoglucanase specific for xyloglucan is preferably substantially devoid of activity towards β-glucan and/or exhibits at the most 25% such as at the most 10% or about 5%, activity towards carboxymethyl cellulose and/or Avicell when the activity towards xyloglucan is 100%. In addition, endoglucanase specific for xyloglucan of the invention is preferably substantially devoid of transferase activity, an activity which has been observed for most endoglucanases specific for xyloglucan of plant origin.

Endoglucanase specific for xyloglucan may be obtained from the fungal species *A. aculeatus*, as described in WO 94/14953. Microbial endoglucanases specific for xyloglucan has also been described in WO 94/14953. Endoglucanases specific for xyloglucan from plants have been described, but these enzymes have transferase activity and therefore must be considered inferior to microbial endoglucanses specific for xyloglucan whenever extensive degradation of xyloglucan is desirable. An additional advantage of a microbial enzyme is that it, in general, may be produced in higher amounts in a microbial host, than enzymes of other origins.

The xyloglucanase, when present, is incorporated into the treating compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the bleaching composition at levels from 0.0001% to 2% of active enzyme by weight of the bleaching composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic bleaching compositions is also disclosed in WO 93/07263 and WO 93/07260 to Genencor International,

WO 89/08694 to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981.

Enzyme Stabilizers - Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 to Novo. The enzymes employed herein can be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Suitable enzyme stabilizers and levels of use are described in U.S. Pat. No. 5,576,282.

Other Detergent Ingredients - The bleaching compositions herein may also optionally contain one or more of the following: polymeric dispersing agents, clay soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, perfumes, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids and/or pigments. Suitable examples of such other detergent ingredients and levels of use are found in U.S. Patent No. 5,576,282.

Methods of Cleaning - In addition to the methods for cleaning fabrics, dishes and other hard surfaces, and body parts by personal cleansing, described herein, the invention herein also encompasses a laundering pretreatment process for fabrics which have been soiled or stained comprising directly contacting said stains and/or soils with a highly concentrated form of the bleaching composition set forth above prior to washing such fabrics using conventional aqueous washing solutions. Preferably, the bleaching composition remains in contact with the soil/stain for a period of from about 30 seconds to 24 hours prior to washing the pretreated soiled/stained substrate in conventional manner. More preferably, pretreatment times will range from about 1 to 180 minutes.

TEST PROTOCOL I:

General / Parameters: All solutions are maintained at 20 °C. Adjustments of pH as required are accomplished using either sodium carbonate or sulfuric acid as appropriate. All solutions are continuously stirred at 500 rpm, except small (1-5 mL) dye bleaching solution (DBS) aliquots removed to measure absorbance. Absorbance values are measures at the l_{max} of the reference dye solution (RDS). Peracetic acid, 32 wt. % solution in dilute acetic acid is purchased from Aldrich (#26,933-6).

OC is the organic catalyst.

OCS is the organic catalyst containing solution prepared by dissolving 0.010 mmoles (typically about 2-3 mg, depending on the molecular weight) of an organic catalyst (OC) at 20 °C in 5 mL of deionized water immediately prior (within one minute) of the time at which the OCS is added to the base solution. If the organic catalyst is not soluble in 5 mL of deionized water, an additional 5 mL of an organic solvent is added to 5 mL of deionized water to aid in the dissolution of the organic catalyst. Organic solvents used are methanol, ethanol, dimethylformamide, or acetonitrile. If the organic catalyst is not soluble in a 1:1 mixture of deionized water and organic solvent, the organic catalyst is dissolved in 100% organic solvent. If the organic catalyst is found to be insoluble in the above solvent media, the organic catalyst is added to the base solution in pure form.

BS is the base solution to which the OCS is added. The base solution is prepared by mixing 1.0 L of deionized water with 10 mg (10 ppm) of a chelant (capable of sequestering transition metal ions in order to avoid decomposition of peracetic acid and/or bleaching species) and a sufficient quantity of sodium carbonate such that upon the addition of 76 mg (76 ppm, 1.0 mmol) of peracetic acid (based on 100% activity), the solution pH is between 9.9 and 10.1. At one minute of stirring, the BS preparation is complete.

OCBS is the organic catalyst containing base solution prepared by the addition of the OCS to 1 L of the just prepared BS. Upon addition of OCS to BS, the OCBS preparation is complete. The OCBS should now have a pH of 10.0 (between 9.9 and 10.1). If the pH is not within this range, the OCBS preparation will need to be repeated, such that the addition of the OCS to the BS is performed along with the addition of sodium carbonate or sulfuric acid in a manner that results in the preparation of an OCBS with a pH of 10.0 (between 9.9 and 10.1).

CDS is the concentrated dye solution, defined as a 90 ppm solution of Tropaeolin O dye (Aldrich 19,968-0) in deionized water at pH 10.

DBS is the dye bleaching solution formed from the addition of a 100 mL aliquot of the OCBS to 10 mL of CDS. The DBS should have an initial pH of 10.0. If (in the unlikely event) the pH of the DBS drops below 9.6 at time = t_D (defined below), the pH must be controlled such that during the interval t_D the pH must remain between 9.8 and 10.1.

w_{OC} is a parameter in the final test protocol used to describe the weight of organic catalyst (OC), based on 100% purity, used to form the organic catalyst solution (OCS). The default value of the parameter is 0.010 mmoles, added to 1.0 L of BS.

Determination of A_{max}. 100 mL of deionized water at pH 10 is added to 10 mL of CDS. The absorbance of the resulting homogeneous reference dye solution (RDS) determined by UV-Visible Spectroscopy at the l_{max} (approximately 518 nm) is A_{max}. The RBS should have a pH of 10.0.

d_{dec} is a parameter in the test protocol describing the time that elapses between the formation of the OCBS and the formation of the dye bleaching solution (DBS) via the addition of the OCBS to the CDS. This value is the decomposition duration of the organic catalyst in the OCBS prior to addition to the CDS. The default value of the parameter d_{dec} (e.g., d_{dec} = 15 min) is defined in the claim set. The value of the parameter d_{dec} is defined to be equal to the value of the parameter d_{ref}.

d_{ref} is a parameter in the test protocol describing the time that elapses between the completion of the BS preparation and the formation of the dye bleaching solution (DBS) via the addition of the BS to the CDS. This value is the reference duration of peracid in the BS prior to addition to the CDS. The default value of the parameter d_{ref} (e.g., d_{ref} = 15 min) is defined in the claim set. The value of the parameter d_{ref} is defined to be equal to the value of the parameter d_{dec}.

d_{bleach} is a parameter in the test protocol describing the time that elapses between the formation of the dye bleaching solution (DBS) and data acquisition. This value is the bleaching duration of the DBS formed from either the addition of BS or OCBS to the CDS. The default value of the parameter d_{bleach} is 5 min.

Test Protocol (Part I):

The initial step is the preparation of the BS as described. The time of completion of the BS preparation is set to t = 0. A 100 mL aliquot of the BS is withdrawn at d_{ref} and added all at once to 10.0 mL of CDS. A 1-5 mL aliquot, R, of the resulting DBS is withdrawn immediately prior to the absorbance determination (data acquisition). Absorbance of R is measured at the l_{max} at the conclusion of d_{bleach}.

The time at which the absorbance determination (data acquisition) of aliquot R is measured is defined as t_R. Therefore, it is required that $t_R = d_{ref} + d_{bleach}$. The absorbance value measured at t_R is defined as $A_{t(R)}$. The symbol $dA_{t(R)}$ is defined as $A_{max} - A_{t(R)}$.

Test Protocol (Part II):

The initial step is the preparation of the OCBS as described. The time of completion of the OCBS preparation is set to t = 0. A 100 mL aliquot of the OCBS is withdrawn at d_{dec} and added all at once to 10.0 mL of CDS. A 1-5 mL aliquot, D, of the resulting DBS is withdrawn immediately prior to the absorbance determination (data acquisition). Absorbance of D is measured at the l_{max} at the conclusion of d_{bleach}.

The time at which the absorbance determination (data acquisition) of aliquot D is measured is defined as t_D. Therefore, it is required that $t_D = d_{dec} + d_{bleach}$. The absorbance value measured at t_D is defined as $A_{t(D)}$. The symbol $dA_{t(D)}$ is defined as $A_{max} - A_{t(D)}$.

Organic catalyst lifetime (OCL) is defined as the value of d_{dec} (or the time the OC spends in the OCBS) such that the value of $dA_{t(D)} = 3 \times dA_{t(R)}$

Two cases exist, depending upon the values of $dA_{t(D)}$ compared to the value of $dA_{t(R)}$.

Case A: If for the lower limit (e.g., 30 seconds) of organic catalyst lifetime the value of $dA_{t(D)}$ [3] $3 \times dA_{t(R)}$, and for the upper limit (e.g., 15 minutes) of organic catalyst lifetime the value of $dA_{t(D)}$ £ $3 \times dA_{t(R)}$ then a fast-acting organic catalyst is indicated, and the OC falls within the boundaries of this invention.

Case B: If for the lower limit (e.g., 30 seconds) of organic catalyst lifetime the value of $dA_{t(D)} < 3 \times dA_{t(R)}$, or for the upper limit (e.g., 15 minutes) of organic catalyst lifetime the value of $dA_{t(D)} > 3 \times dA_{t(R)}$ then a fast-acting organic catalyst is not indicated, and the OC falls within the boundaries of this invention.

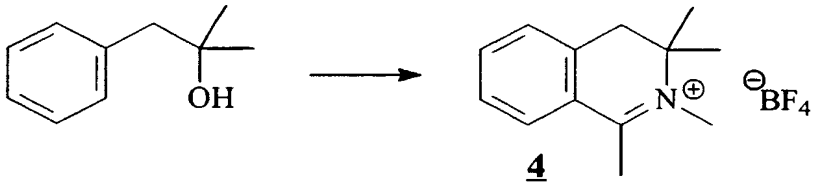
An organic catalyst compound that exhibits an organic catalyst lifetime of from 15 seconds to 15 minutes is defined as a fast-acting organic catalyst compound selected from the group consisting of those in which the value of $dA_{t(D)} \leq 3 \times dA_{t(R)}$ at the conclusion of d_{bleach}, wherein for example d_{dec} = 15 minutes; **and** the value of $dA_{t(D)} \geq 3 \times dA_{t(R)}$ at the conclusion of d_{bleach}, wherein for example d_{dec} = 15 seconds.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the following examples some abbreviations known to those of ordinary skill in the art are used, consistent with the disclosure set forth herein.

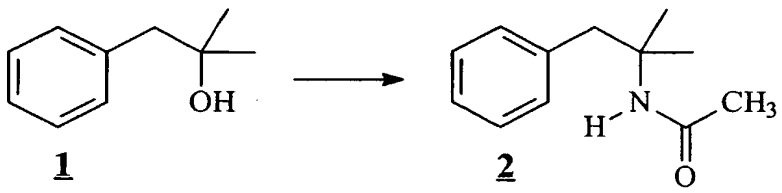
EXAMPLE I

Preparation of 1,3,3-trimethyl-3,4-dihydroisoquinolinium tetrafluoroborate(**4**):



4

Step 1: Preparation of *N*-acetyl-α,α-dimethyl-β-phenethylamine (**2**):

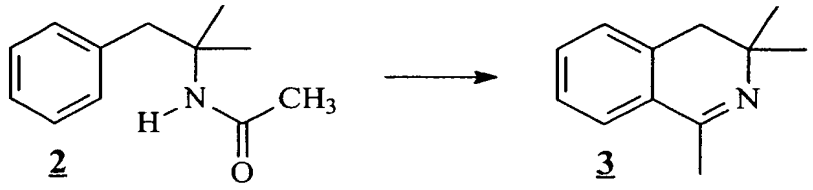


1 **2**

To CH_3CN (12.3 g, 0.3 mol) in a 250 mL three-necked round-bottom flask equipped with thermometer and adapter, mechanical stirrer, reflux condenser, ice bath and pressure equalizing addition funnel is added slowly (WARNING! Very SLOW addition, at or below 10 °C, is

necessary to avoid splattering) concentrated H_2SO_4 (29.4 g, 0.3 mol). To the mixture of CH_3CN and H_2SO_4 is added slowly (keeping the temperature at or below 10 °C) 10 mL of glacial acetic acid. The ice bath is removed and the mixture is stirred rapidly as 2-methyl-1-phenyl-2-propanol (0.30 mol) is added over 5 min, while keeping the temperature of the solution at or below 60 °C (via cooling bath). The solution is allowed to stir at room temperature for 3 days. The viscous oil is poured into ice (500 g) with the aid of water (150 mL), CH_2Cl_2 (50 mL), and a 10% NH_4OH solution (150 mL). The lower organic layer is separated, and the aqueous layer is washed with CH_2Cl_2 (100 mL), and the combined organic layers are washed with brine, dried over $MgSO_4$ and concentrated. The solid is recrystallized from ether / CH_2Cl_2 to give 3.

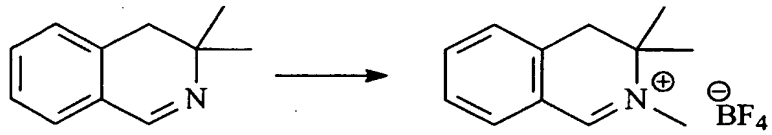
Step 2: Preparation of 1,3,3-trimethyl-3,4-dihydroisoquinoline (4):



2 3

Typical procedure for the synthesis of dihydroisoquinoline is as described in the art, as in Larsen, R. D. et. al. *J. Org. Chem.* **1991**, *56*, 6034. The described procedure is used for the conversion of the amide 2 to 1,3,3-trimethyl-3,4-dihydroisoquinoline (3). The crude product is purified by Kugelrohr distillation (0.25 mm Hg / 100 - 110 °C) to give 3 as a light yellow oil.

Step 3: Preparation of 1,3,3-trimethyl-3,4-dihydroisoquinoliniume tetrafluoroborate (4):

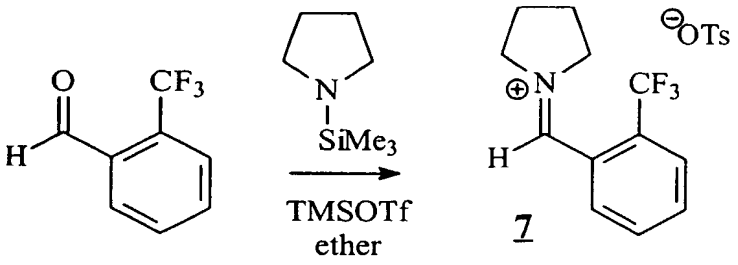


3 4

A round-bottom flask equipped with magnetic stir bar at 0 °C is charged with trimethyloxonium tetrafluoroborate (Meerwein salt, 1.13 g, 7.7 mmol) and methylene chloride (15 mL). To the stirred solution is added a solution of 1,3,3-trimethyl-3,4-dihydroisoquinoline (3, 1.21 g , 7.0 mmol) in methylene chloride (40 mL) over a period of 5 min. The heterogeneous solution is allowed to warm to room temperature, and stirred overnight. The solution is concentrated to give 4. The lifetime (OCL) of 4 was determined using the above Test Protocol to be about 5 min.

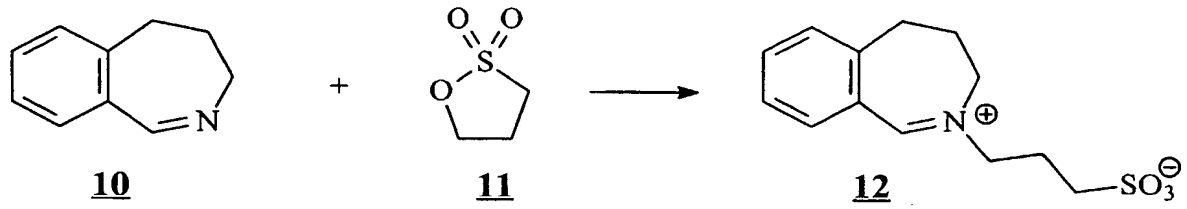
EXAMPLE III

Preparation of *ortho*-triflouromethyl iminium tosylate salt (7):



The procedure for the synthesis of 7 is as described in the art, as in Armstrong, A. et. al. *Synlett* **1997**, 1075. The lifetime (OCL) of 7 was determined using the above Test Protocol to be approximately 1 min.

EXAMPLE IV



10 **11** **12**

Preparation of 2-(3-sulfonato)propyl-4,5-dihydro-3H-2-benzazepine (12):

A 100 mL round-bottom flask equipped with magnetic stir bar and distillation apparatus is charged with 3-phenylpropylamine (24.8 g, 0.18 mol) and 88% formic acid (41.4 g, 0.79 mol, 4.4 equiv.) and the reaction is distilled at 150 °C. Beginning after one hour, additional 8 ml aliquots of 88% formic acid are added over a 2 h period until the 3-phenylpropylamine is consumed, as monitored by gas chromatography. The reaction mixture is distilled (using a Dean-Stark trap) at 200 °C for 3 hours after which it is allowed to cool to room temperature.

A 500 mL round-bottom flask equipped with overhead mechanical stirrer, reflux condenser, and addition funnel is charged with phosphorus pentoxide (38.6 g) and polyphosphoric acid (168 g). The mixture is stirred and heated at 180 °C for about 8 h, then cooled to 150 °C. The cooled, crude 3-phenylpropylformamide prepared as described above is added dropwise to this mixture. On complete addition the reaction is heated and stirred at 170 °C overnight. The mixture is

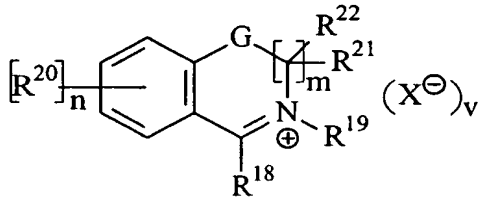
cooled to room temperature and diluted with ice water (1.0 L), washed with diethyl ether (500 mL) and cooled in a brine/ice bath while the pH is adjusted to 9 with saturated potassium hydroxide. The aqueous solution is extracted with ether (2 x 250 mL) and the pooled organics are dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield an oil which solidifies upon addition of ether/hexane, and filtered to give 4,5-dihydro-3H-2-benzazepine, **10**.

A 250 mL round-bottomed flask equipped with magnetic stir bar, argon inlet, addition funnel, and reflux condenser is charged with 4,5-dihydro-3H-2-benzazepine (**10**, 1.45 g, 10.0 mmol) and acetonitrile (10 mL). This mixture is cooled in an ice bath and charged dropwise with a solution of 1,3-propane sultone (1.34 g, 11.0 mmol) in acetonitrile (5 mL). On complete addition the ice bath is removed and the reaction is heated to reflux overnight. The mixture is allowed to cool to room temperature and volatiles are removed under reduced pressure. The solid 2-(3-sulfonato) propyl-4,5-dihydro-3H-2-benzazepine (**12**) is slurried and rinsed with acetone, and allowed to air dry.

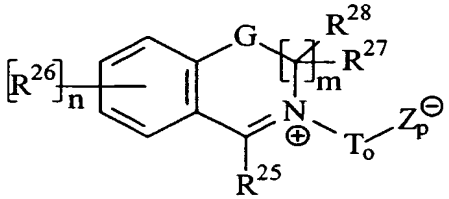
The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the following examples some abbreviations known to those of ordinary skill in the art are used, consistent with the disclosure set forth herein.

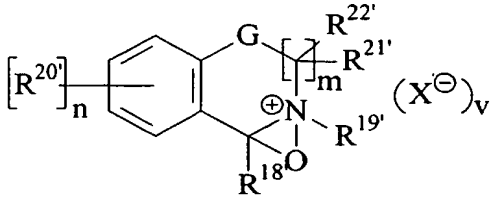
The organic catalyst in the following examples can be any of the organic catalysts described hereinbefore including Examples I-IV, preferably the organic catalysts are represented by the following structures (with substituent groups defined above).

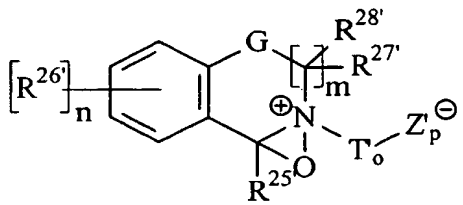


[XI]

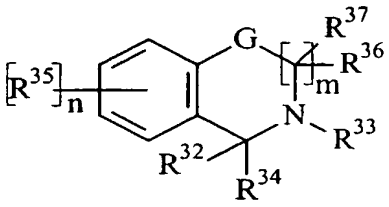


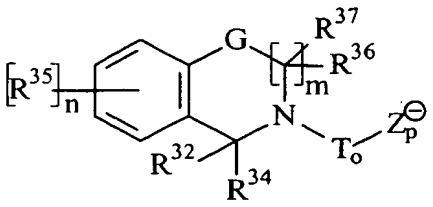
[XII]



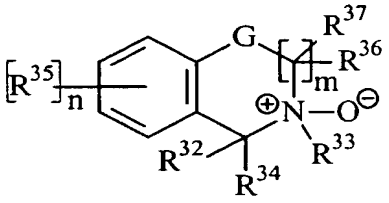


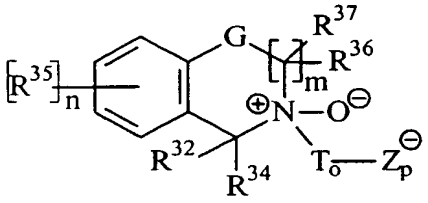
[XIII] [XIV]



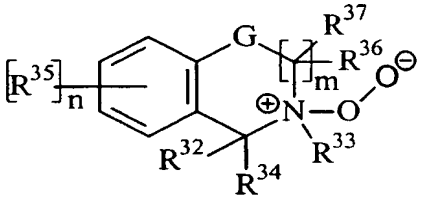


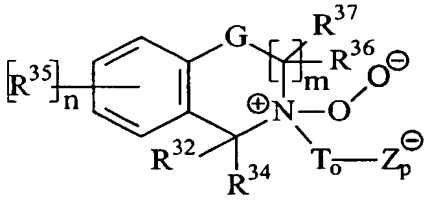
[XV] [XVI]





[XVII] [XVIII]





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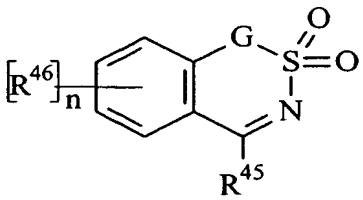
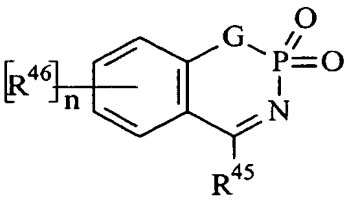
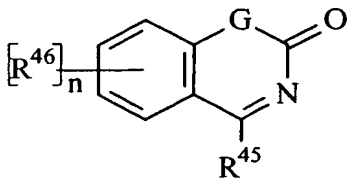
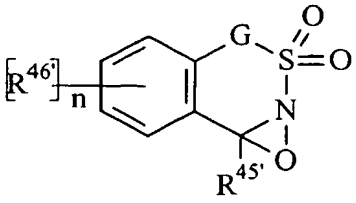


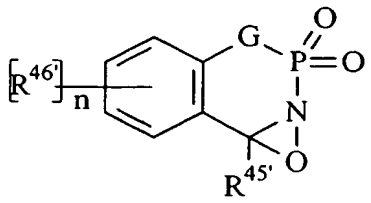




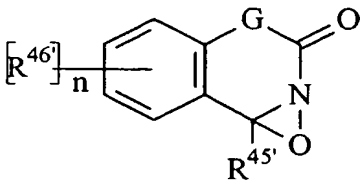
[XXVIIIa] [XXVIIIb] [XXIX]



[XXXIa]

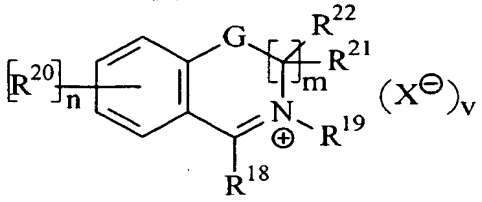


[XXXIb]

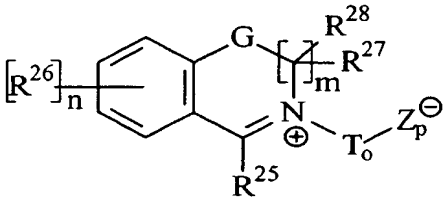


[XXXII]

Preferably the organic catalysts are iminium-based organic catalysts, as represented by the following structures (with substituent groups defined above).



[XI]



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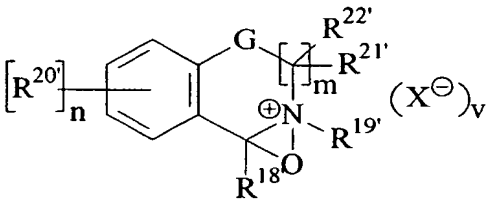
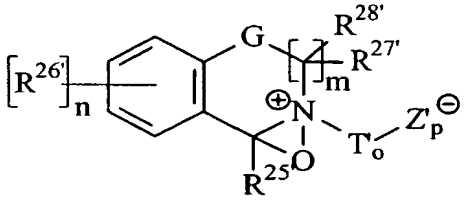


[XIII]



[XIV]

EXAMPLE V

Bleaching detergent compositions having the form of granular laundry detergents are exemplified by the following formulations.

	A	B	C	D	E
Organic Catalyst *	0.14	0.40	0.14	0.20	0.07
Sodium Percarbonate	5.30	0.00	0.00	4.00	0.00
Sodium Perborate Monohydrate	0.00	5.30	3.60	0.00	4.30
Linear Alkylbenzenesulfonate	12.00	0.00	12.00	0.00	21.00

C45AE0.6S	0.00	15.00	0.00	15.00	0.00
C2 Dimethylamine N-Oxide	0.00	2.00	0.00	2.00	0.00
C12 Coco Amidopropyl Betaine	1.50	0.00	1.50	0.00	0.00
Palm N- Methyl Glucamide	1.70	2.00	1.70	2.00	0.00
C12 Dimethylhydroxyethyl-ammonium Chloride	1.50	0.00	1.50	0.00	0.00
AE23-6.5T	2.50	3.50	2.50	3.50	1.00
C25E3S	4.00	0.00	4.00	0.00	0.00
Conventional Activator (NOBS)	0.00	0.00	0.60	0.00	0.00
Conventional Activator (TAED)	2.00	2.80	2.00	1.80	2.30
Sodium Tripolyphosphate	25.00	25.00	15.00	15.00	25.00
Zeolite A	0.00	0.00	0.00	0.00	0.00
Acrylic Acid / Maleic Acid Copolymer	0.00	0.00	0.00	0.00	1.00
Polyacrylic Acid, partially neutralized	3.00	3.00	3.00	3.00	0.00
Soil Release Agent	0.00	0.00	0.50	0.40	0.00
Carboxymethylcellulose	0.40	0.40	0.40	0.40	0.40
Sodium Carbonate	2.00	2.00	2.00	0.00	8.00
Sodium Silicate	3.00	3.00	3.00	3.00	6.00
Sodium Bicarbonate	5.00	5.00	5.00	5.00	5.00
Savinase (4T)	1.00	1.00	1.00	1.00	0.60
Termamyl (60T)	0.40	0.40	0.40	0.40	0.40
Lipolase (100T)	0.12	0.12	0.12	0.12	0.12
Carezyme(5T)	0.15	0.15	0.15	0.15	0.15
Diethylenetriaminepenta (methylenephosphonic Acid)	1.60	1.60	1.60	1.60	0.40
Brightener	0.20	0.20	0.20	0.05	0.20
Sulfonated Zinc Phthalocyanine Photobleach	0.50	0.00	0.25	0.00	0.00
$MgSO_4$	2.20	2.20	2.20	2.20	0.64
Na_2SO_4	balance	balance	balance	balance	balance

*Organic catalyst can be any of the organic catalysts described herein, preferably it is an iminium-based organic catalyst, more preferably it is a dihydroisoquinolinium-based organic catalyst.

Any of the above compositions is used to launder fabrics at a concentration of 3500 ppm in water, 25°C, and a 15:1 water:cloth ratio. The typical pH is about 9.5 but can be can be adjusted by altering the proportion of acid to Na- salt form of alkylbenzenesulfonate.

EXAMPLE VI

Bleaching detergent compositions having the form of granular laundry detergents are exemplified by the following formulations.

	A	B	C	D	E
Organic Catalyst *	0.06	0.34	0.14	0.14	0.20
Sodium Percarbonate	5.30	0.00	0.00	0.00	0.00
Sodium Perborate Monohydrate	0.00	9.00	17.60	9.00	9.00
Linear Alkylbenzenesulfonate	21.00	12.00	0.00	12.00	12.00
C45AE0.6S	0.00	0.00	15.00	0.00	0.00
C2 Dimethylamine N-Oxide	0.00	0.00	2.00	0.00	0.00
C12 Coco Amidopropyl Betaine	0.00	1.50	0.00	1.50	1.50
Palm N- Methyl Glucamide	0.00	1.70	2.00	1.70	1.70
C12 Dimethylhydroxyethylammonium Chloride	1.00	1.50	0.00	1.50	1.50
AE23-6.5T	0.00	2.50	3.50	2.50	2.50
C25E3S	0.00	4.00	0.00	4.00	4.00
Conventional Activator (NOBS)	0.00	0.00	0.00	1.00	0.00
Conventional Activator (TAED)	1.80	1.00	2.50	3.00	1.00
Sodium Tripolyphosphate	25.00	15.00	25.00	15.00	15.00
Zeolite A	0.00	0.00	0.00	0.00	0.00
Acrylic Acid / Maleic Acid Copolymer	0.00	0.00	0.00	0.00	0.00

Polyacrylic Acid, partially neutralized	0.00	3.00	3.00	3.00	3.00
Soil Release Agent	0.30	0.50	0.00	0.50	0.50
Carboxymethylcellulose	0.00	0.40	0.40	0.40	0.40
Sodium Carbonate	0.00	2.00	2.00	2.00	2.00
Sodium Silicate	6.00	3.00	3.00	3.00	3.00
Sodium Bicarbonate	2.00	5.00	5.00	5.00	5.00
Savinase (4T)	0.60	1.00	1.00	1.00	1.00
Termamyl (60T)	0.40	0.40	0.40	0.40	0.40
Lipolase (100T)	0.12	0.12	0.12	0.12	0.12
Carezyme(5T)	0.15	0.15	0.15	0.15	0.15
Diethylenetriaminepenta(methylenephosphonic Acid)	0.40	0.00	1.60	0.00	0.00
Brightener	0.20	0.30	0.20	0.30	0.30
Sulfonated Zinc Phthalocyanine Photobleach	0.25	0.00	0.00	0.00	0.00
$MgSO_4$	0.64	0.00	2.20	0.00	0.00
Na_2SO_4	balance	balance	balance	balance	balance

*Organic catalyst can be any of the organic catalysts described herein, preferably it is an iminium-based organic catalyst, more preferably it is a dihydroisoquinolinium-based organic catalyst.

Any of the above compositions is used to launder fabrics at a concentration of 3500 ppm in water, 25°C, and a 15:1 water:cloth ratio. The typical pH is about 9.5 but can be can be adjusted by altering the proportion of acid to Na- salt form of alkylbenzenesulfonate.

EXAMPLE VII

A bleaching detergent powder in accordance with the present invention comprises the following ingredients:

Component	Weight %
Organic Catalyst*	0.07
TAED	2.0
Sodium Perborate Tetrahydrate	10
C_{12} linear alkyl benzene sulfonate	8
Phosphate (as sodium tripolyphosphate)	9

Sodium carbonate	20
Talc	15
Brightener, perfume	0.3
Sodium Chloride	25
Water and Minors	Balance to 100%

*Organic catalyst can be any of the organic catalysts described herein, preferably it is an iminium-based organic catalyst, more preferably it is a dihydroisoquinolinium-based organic catalyst.

EXAMPLE VIII

A laundry bar suitable for hand-washing soiled fabrics is prepared by standard extrusion processes and comprises the following:

Component	Weight %
Organic Catalyst*	0.2
TAED	1.7
NOBS	0.2
Sodium Perborate Tetrahydrate	12
C_{12} linear alkyl benzene sulfonate	30
Phosphate (as sodium tripolyphosphate)	10
Sodium carbonate	5
Sodium pyrophosphate	7
Coconut monoethanolamide	2
Zeolite A (0.1-10 micron)	5
Carboxymethylcellulose	0.2
Polyacrylate (m.w. 1400)	0.2
Brightener, perfume	0.2
Protease	0.3
$CaSO_4$	1
$MgSO_4$	1
Water	4
Filler[2]	Balance to 100%

*Organic catalyst can be any of the organic catalysts described herein, preferably it is an iminium-based organic catalyst, more preferably it is a dihydroisoquinolinium-based organic catalyst.
[2] Can be selected from convenient materials such as $CaCO_3$, talc, clay, silicates, and the like. Acidic fillers can be used to reduce pH.

EXAMPLE IX

A laundry detergent composition suitable for machine use is prepared by standard methods and comprises the following composition:

Component	Weight%
Organic Catalyst*	0.82
TAED	7.20
Sodium Perborate Tetrahydrate	9.2
Sodium Carbonate	23.74
Anionic surfactant	14.80
Alumino Silicate	21.30
Silicate	1.85
Diethylenetriaminepentacetic acid	0.43
Polyacrylic acid	2.72
Brightener	0.23
Polyethylene glycol solids	1.05
Sulfate	8.21
Perfume	0.25
Water	7.72
Processing aid	0.10
Miscellaneous	0.43

*Organic catalyst can be any of the organic catalysts described herein, preferably it is an iminium-based organic catalyst, more preferably it is a dihydroisoquinolinium-based organic catalyst.

The composition is used to launder fabrics at a concentration in solution of about 1000 ppm at a temperature of 20-40°C and a water to fabric ratio of about 20:1.

EXAMPLE X

Component	Weight%
Organic Catalyst*	1.0

TAED	10.0
Sodium Perborate Tetrahydrate	8.0
Sodium Carbonate	21.0
Anionic surfactant	12.0
Alumino Silicate	18.0
Diethylenetriaminepentacetic acid	0.3
Nonionic surfactant	0.5
Polyacrylic acid	2.0
Brightener	0.3
Sulfate	17.0
Perfume	0.25
Water	6.7
Miscellaneous	2.95

*Organic catalyst can be any of the organic catalysts described herein, preferably it is an iminium-based organic catalyst, more preferably it is a dihydroisoquinolinium-based organic catalyst.

While particular embodiments of the subject invention have been described, it will be obvious to those skilled in the art that various changes and modifications of the subject invention can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the invention.

The composition is used as a laundry auxiliary for laundering fabrics at a concentration in solution of about 850 ppm at a temperature of 5-50°C and a water to fabric ratio of about 20:1.

The compositions of the present invention can be suitably prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. Patent Nos. 5,691,297; 5,574,005; 5,569,645; 5,565,422; 5,516,448; 5,489,392; and 5,486,303.

In addition to the above examples, the bleaching compositions of the present invention can be formulated into any suitable laundry detergent composition, non-limiting examples of which are described in U.S. Patent Nos. 5,679,630; 5,565,145; 5,478,489; 5,470,507; 5,466,802; 5,460,752; 5,458,810; 5,458,809; and 5,288,431.

Having described the invention in detail with reference to preferred embodiments and the examples, it will be clear to those skilled in the art that various changes and modifications may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.